THE
SCIENTIFIC PRINCIPLES OF PLANT PROTECTION
WITH SPECIAL REFERENCE TO
CHEMICAL CONTROL

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BY

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PREFACE

Entomology and Mycology are concerned with the organisms responsible for injury and disease among crop plants, but the problems of the control of crop pests—Plant Protection—involve not only biological but equally important chemical and physical studies. Indeed, so extensive has the field become that co-operation between the entomologist or mycologist and the chemist, physicist or plant physiologist is recognized as the most economical and successful method of progress. The primary purpose of this book is to assist this co-operation by a survey of the scientific principles underlying modern methods of control of crop pests.

Advisory officers and research workers in Plant Pathology find that the literature of Plant Protection is scattered and, moreover, that the discussion of control measures of any particular fungus or pest is frequently overshadowed by purely biological data. Yet the principles underlying these control measures permit of classification and co-ordinated discussion.

As successful control is based only upon accurate knowledge of the life-history and habits of the organism responsible, the Advisory officer is rightly recruited from biologists. He is therefore better acquainted with the biological than with the physico-chemical aspects of Plant Protection. For this reason, the latter aspects are dealt with in greater detail, though it is hoped that this emphasis will not be misinterpreted as an implication of the greater importance of chemical over biological and cultural methods of control. The object has been to present to the mycologist and entomologist a detailed survey of the physico-chemical factors and to provide the chemist and physicist with a means of approach to the biological side.

A second purpose has been to provide a book of reference on Insecticides and Fungicides. The chemistry of these materials is a young science, but, following the success of chemotherapeutics, the interest of the chemical manufacturer has been attracted to this field. Already the range of chemicals available for the purposes of Plant Protection has been widely extended. Special atten-

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tion has therefore been paid to the mode of action of pest control materials and to the relationships between chemical constitution and toxicity and, for the first time, it has been possible to confine examples to the realm of Phytopathology.

The details of actual methods of insecticide and fungicide application used in practice, including also the agricultural engineering problems, have formed the subject of bulletins and leaflets in the different countries of the world. As they must vary with the conditions found in those countries their applicability is limited and, except where examples have been found useful, such practical details have not been mentioned. Nor has the inclusion of the principles underlying the control of non-parasitic diseases been possible. A discussion of these diseases, due in a broad sense to unfavourable soil and climatic conditions, would involve a consideration of nutritional and environmental factors beyond the scope of a single volume.

The present edition therefore follows the plan of the second edition but, in order to include a discussion of the many developments of the subject within the past four years, a drastic pruning of the text was necessary. The book has been reset for this, the third edition. The subjects in which the greatest advance has been made include the nature and control of virus diseases, the epidemiological factors determining the degree of attack and the interpretation, to practical conditions, of the results of the laboratory assessment of the qualities which determine insecticidal and fungicidal efficiency. With knowledge of the reasons for the efficiency of the old-established but empirically-discovered insecticides and fungicides, it has become possible to compound both new and old toxic products to simple, fool-proof pest control materials. The end of the home-made insecticide or fungicide and its replacement by the compounded product is in sight.

The author acknowledges with gratitude the continued interest of Sir Daniel Hall in the book. He gladly tenders his thanks to the colleagues of the Long Ashton Research Station for their advice and patient help ; in particular, to Mr. R. W. Marsh, whose comments and criticisms in the revision of the manuscript were invaluable. The interest of many correspondents who have supplied historical data not available in the literature or who have suggested improvements to the book has been the greatest encouragement to its author. Finally he is happy to record the value of the abstracts now provided by the Imperial Bureaux of

Entomology, of Mycology and of Horticulture and Plantation Crops, the use of which enabled a rapid sifting, from an enormous amount of literature, of the papers of special value for his purpose.

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THE SCIENTIFIC PRINCIPLES OF
PLANT PROTECTION

CHAPTER I

INTRODUCTION

The concept of a " struggle for existence " among living organisms has as a corollary the idea of a " natural balance." Considering an individual plant, the continuation of the species will depend upon its ability to reach maturity and to provide for the reproduction of its kind despite the many factors which tend towards its suppression. Of these factors, an important group comprises those other organisms, the pests of the plant, which in the course of their existence cause direct injury or prejudice its successful development. If the plant tends towards an increase, conditions will favour the multiplication of the pests ; the increase of the pests brings about, in turn, a reduction of the productivity of the plant. These processes result in the establishment of an equilibrium—the " natural balance."

Man is able to modify this natural balance to suit better his own needs. He is able to encourage artificially the growth and reproduction of those plants useful to him as crop plants and to discourage the growth and reproduction of those particular pests which, because of that encouragement, tend likewise to increase. It is because of this tendency to increase—the fact that the improvement of growth conditions of the crop plant simultaneously provides improved conditions for the growth of the pests—that there arises the need for methods of plant protection.

If wheat, for example, grew only as isolated plants among other vegetation, the chance of survival of the spore of the fungus to which Smut of wheat is due would be meagre and the fungus would play but an unimportant rôle in the determination of the chance of survival of the wheat. But when wheat is cultivated as a crop, not

only is the spore of the Smut fungus more certain to find a suitable host, but the conditions for the multiplication and spread of the fungus are rendered so favourable that it may become a factor of primary importance in the determination of the yield of the wheat crop.

Prior to 1850, the small highly coloured beetle, now known as the Colorado Beetle, was an unknown and insignificant insect feeding upon the wild potato and other solanaceous plants of the Rocky Mountains. The settler, who brought with him and who planted the cultivated potato, innocently supplied the beetle, not only with an abundance of suitable food, but with the means whereby to extend its activities. From 1850 onwards, the beetle has slowly spread from its original home ; by 1859 it had reached Nebraska, by 1870 it had travelled as far north as Ontario, and by 1874, continuing its career, it had reached the Atlantic coast.

Prior to 1922 sporadic outbreaks occurred on a few occasions in Europe, but prompt eradicative measures, with one exception, succeeded in preventing the establishment of the beetle. In 1922 colonies of the beetle were found in the Gironde district of France, and although by energetic action the outbreak was held in check until 1927, the area infested has since grown at an alarming rate.

The beetle is now established throughout France, Luxemburg, Belgium, Holland, Switzerland and the parts of Germany adjacent to these countries. The control of the pest is the subject of extensive research in all potato-growing countries, work which is co-ordinated by a special international committee which has put forward (1) standard proposals for the search for and treatment of new centres of infection and for control in regions where the Colorado Beetle is established.

The history of agriculture abounds with examples of this dire result of man's interference with the original natural balance, yet it is only within recent years that the study of the protection of plants from their enemies in the plant and animal world has received scientific attention. This delay arises without doubt from the belated recognition of the causative agents of what were previously considered uncontrollable disorders. The larger organisms, the higher plants and animals, are automatically controlled to a great extent by the processes of cultivation and of civilization. The smaller of these organisms, unknown to the early husbandman, have only within recent years been recognized and studied. It is with the steady and continued realization of the nature of plant diseases,

that the possibilities and importance of plant protection have increased.

The urgency of the need for methods of control of the harmful organic factors which contribute to the limitation of crop yield has increased from yet other aspects. In nature, as a result of the struggle for existence, the tendency will be for the evolution of a variety of plant whose reproductive powers are delicately balanced by its ability to withstand the attack of pests. By cultivation, however, varieties are produced capable of high productivity yet but partially resistant or even susceptible to the attack of pests. Indeed it may be said that in general the heavier cropping and more specialized varieties of plants are more adversely affected by the activities of other organisms. Again, present knowledge of the soil and nutrient factors of crop production is such that the grower is able so to modify and control them that he secures the most profitable yield. It becomes all the more important therefore that he should be able to control the biological factors in a similar manner.

The study of plant protection, the control of the plant's pests, may then be granted an importance no less fundamental to the study of crop production than that of the questions of soil tillage—agriculture in its primary sense—and that of the questions of plant nutrition.

Reviewing briefly the status of the organisms which may be classed as the plant's pests, representatives are found from the whole range of the plant and animal kingdoms.

Of the plant kingdom, there are first those of the higher plants whose presence is detrimental to the development of the crop, classed under the general term of " weed." The methods of soil preparation, of sowing and of soil tillage after sowing, are designed, not only to improve the growth conditions of the crop, but also to reduce the injury to the crop occasioned by weeds. In this sense, cultivation is perhaps the most important of the methods of pest control. There are further to be considered those of the higher plants (Spermatophytes), such as the Dodders (*Cuscuta* spp.), which are true parasites in that they derive all or part of their food direct from the living plant.

Descending the scale, of the algæ but few species are of importance. The fungi are, however, in the front rank of the plant's pests.

Botanically, the fungi (Eumycetes) are cellular plants differing from the algæ in their complete lack of chlorophyll or chromato-

phores. For this reason, the fungi are unable to build up the food
they require from the constituents of soil, air and water as do green
plants, but, in order to live, must feed upon organic matter, either
in the form of decaying plant or animal remains (Saprophytic
fungi), or in the form of living plant or animal matter (Parasitic
fungi). Of the Myxomycetes or " Slime Fungi " certain members,
such as *Plasmodiophora brassicæ* causing the Club Root of cruciferous
plants, need consideration. At the lower end of the scale are the
Schizomycetes or bacteria, which are now recognized as the causa-
tive agents of an ever-increasing number of diseases, not only
among plants but among human beings and animals.

These three latter groups, the Eumycetes, the Myxomycetes and
the Bacteria, were formerly all classed as fungi. This older classi-
fication is often retained, as in the word Fungicide, a chemical toxic
to these organisms, and a term used to embrace a wide range
of such substances employed for the control of these particular
pests.

Animals are, for their food supply, entirely dependent, either
directly or indirectly, upon the plant world. " Green " plants,
which are able, because of the presence of chlorophyll or related
pigments in their tissue, to synthesize organic matter from carbon
dioxide and the nutrient materials present in the soil and water,
are the primary source of energy in its widest sense. All animals
may indeed be regarded as pests of the plant, the most noxious of
which, from the plant's point of view, is Man.

Of the higher animals, the Vertebrates, there are special cases
where civilization has not entirely controlled those injurious to
crops. The question of whether any species of bird causes, in the
long run, any serious damage to crops, is controversial. Rodents,
such as voles, rats, and rabbits, may sometimes cause injury through
their abnormal abundance. The ravages of these pests are also
serious in orchards or vineyards, which represent a long-term
investment for their owners.

Of the Invertebrates, the Arthropods form a group of great
importance as plant pests in that it includes the true Insects,
animals having three pairs of legs and whose adult body consists
of three parts. The Arachnida, represented by the " Red Spiders "
and other mites, which differ from insects in having no distinct
division of the body into three parts and usually possessing four
pairs of legs, also figure prominently. Of the lower orders of
animals, certain of the Nematodes (thread-like worms, generally

with unsegmented bodies), and possibly of the Protozoa, must be included as plant pests. .

The Arachnida and Insecta are usually classed together in the popular sense of the word " insect." Therefore, in a manner analogous to the use of " Fungicide," the term " Insecticide " is taken to embrace those substances toxic to insects in this wider sense.

This list would be incomplete without mention of viruses. Virus diseases are common to both the animal and plant worlds and are a type of infectious disease of which the causative agent is not made visible by ordinary microscopic methods. In many of their properties, such as their power of multiplication, the viruses resemble organisms, which justifies their inclusion in the catalogue of plant pests. But some of the viruses have now been identified with nucleoproteins, a discovery of absorbing interest which seems to close the gap between the complex organic molecule and the living organism.

The damage caused by the individual species of the list may be but slight or it may be serious enough to threaten or even prevent the cultivation of the attacked plant in localities where the pest is present. The selection of control measures will be guided, in each case, by cost in relation to loss or inconvenience caused by the pest. To give an estimate of the monetary loss due to diseases and pests presents obvious difficulties, but reliable estimates are of staggering dimensions (2). It is doubtful whether the labour involved in compiling such estimates is repaid by their significance for, in their calculation, due weight cannot be given to factors such as the effects of overproduction had the disease or pest not reduced yield and the possibility that nutritional or other factors might have limited yield had the pest not intervened. A more profitable study is of the type carried out by the California Agricultural Experiment Station (3) or by Stevens and Wood (4) on the economic effects of the introduction and use of plant protection. Probably the greatest economic benefit of plant protection is the additional powers it confers on producers to control and stabilize production. The plum or hop grower need no longer gamble his livelihood on the weather being unfavourable to the aphides infesting his crop. The potato grower is now able to curb the violent fluctuations of the potato crop (5) due to Potato Blight, the direct cause of the Irish famine of the 1840's and indirectly responsible for such diverse events as the Repeal of the Corn Laws and, through the

Irish immigrations to the New World, for the preponderance of Irishmen among the police of New York.

Historically the question of pest control is of great antiquity. The importance of the loss caused to the early land-worker by the ravages of an insect such as the locust, is reflected in the story of the plagues of Egypt, whilst it is rather surprising to find the " blasting and mildew " of corn, the result of fungus diseases, recognized in the catalogue of afflictions which, according to the Mosaic law, would befall the evildoer (6).

The Romans, to preserve their fields from " mildew " (probably the Rust of Wheat), held an annual festival—the Robigalia—in honour of the deity Robigus or Robigo, a rite the institution of which is considered to be due to Numa who, according to legend, was the second king of the Romans. As is but to be supposed, more mundane remedies were also employed. Pliny, in his *Historia Naturalis*, Books 17 and 18 (A.D. 77), gave a series of measures for the control of this particular cereal disease. It must be assumed, however, that apart from mechanical methods of dealing with the more obvious insect pests, such early control measures were of a purely rule-of-thumb type. Rational means of control could only arise after the cause of the injury was known.

From this point of view, the history of plant protection is seen to follow closely the history of the scientific study of the organisms which have been described as the plant's enemies. Originally the study of plant diseases—since no responsible organism was recognized—fell to the botanist and was entirely physiological in outlook. Thus, even in 1841, Meyen (7) considered that smut spores were the product of an excessive and abnormal nutrition. The definite recognition of the parasitism of fungi dates from 1853, when Anton de Bary published his classical work upon " die Brandpilze " (8). Thus did plant pathology pass slowly to the realm of mycology, and even the study of the non-parasitic diseases became the work of the applied mycologist. The first general treatise embracing this wider view of plant pathology appeared as a series of articles by Berkeley (9). Later, as a result of the work of Louis Pasteur upon the bacteria and of the introduction of the " plate " method of isolating bacteria by Robert Koch (1881), the existence of bacterial diseases of plants became established, to the credit mainly of Thomas Burrill (1879–81). The proof of the infectious nature of the Mosaic Disease of Tobacco, by Iwanowski in 1892, provided yet a further section for the work of the phytopathologist.

To-day, therefore, plant pathology, phytopathology or applied mycology—the terms are often used as if synonymous—embraces the study of the non-parasitic diseases and those due to faulty cultivation and malnutrition of the plant in addition to that of the parasitic diseases due to fungi and bacteria. Further, the study of the virus diseases, and even of diseases due to animal parasites such as nematodes and protozoa, is part of phytopathology.

So, by the accident of its evolution, plant pathology is frequently considered not to include the study of those diseases due to insects, using the word " insects " in its widest sense. Applied mycology and economic entomology have remained apart, the latter subject embracing not only the control of " insect " pests but also the control of noxious higher animals. The evolution of economic entomology, unlike the development of phytopathology, has proceeded smoothly, a progress in which it is impossible to record outstanding events.

If the development of the study of plant protection were to be traced in a like manner, employing as milestones the prominent events in its history, those events are found to coincide closely with the occurrence of particular epiphytotics. The appearance in Europe of the Powdery Mildew of the Vine (1845) was followed by an extension of the use of sulphur as a fungicide (1848) ; the severe outbreak, in France, of the Downy Mildew of the Vine (1879) was followed by Millardet's discovery of the fungicidal value of the copper sulphate-lime mixture (1882). The spread of the Colorado Beetle (1850-9), which we have mentioned above, was countered by the introduction of Paris Green (1867), an arsenical later displaced by lead arsenate (1892), a material first used in the United States during the Gipsy Moth plague of 1889. The introduction of hydrocyanic acid and the " tent " method of fumigation (1886) followed the rapid spread, in California, of certain scale insects (1886) ; the loss caused by these pests also led to the discovery of the capabilities of biological control (1889).

It is perhaps more interesting to follow the history of the control of one or more particular pests, but as this is the method which has been adopted for the discussion of the chemical methods of seed treatment, it is unnecessary to give further examples.

Any attempt to classify, under definite headings, the various methods now employed in plant protection is rendered difficult, not so much by their complexity as by their interdependence one upon the other. By adopting groups sufficiently wide, it is con-

venient to summarize these methods by the following scheme. The large majority fall into the first group (A) and may be termed—

(**A**) *Preventive*, under which head may be included those methods concerning more directly :

    (1) The Host Plant :

        (*a*) The use of resistant varieties.

        (*b*) Methods by which the plant is covered with a chemical capable of protecting it from attack or of deterring its insect pests.

        (*c*) Methods employing the influence of external factors (climatic and biological) on the susceptibility of the plant to attack.

    (2) The Parasite :

        (*a*) Methods employing the influence of external factors in the activity of the parasite.

        (*b*) The destruction of the parasite either—

            (i) on the " seed "

            (ii) in the soil $\Big\}$ prior to planting.

        (*c*) Mechanical means whereby the parasite is trapped or infection prevented.

        (*d*) The treatment of centres and vectors of infection.

(B) *Curative :* the destruction of the parasite after its attack on the plant is established, by the application of toxic chemicals.

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PLANT RESISTANCE

THE PRODUCTION OF RESISTANT VARIETIES

Nature herself has utilized this method of disease and pest control. The plant is engaged in a continual struggle against its parasitic enemies, and in the course of time those varieties which are the least resistant to their attack will succumb. Those more resistant will survive and beget plants which, possessing the inheritable characteristics inducing resistance, will live to continue the process of natural selection. Man has adapted this natural process, primarily to produce varieties of better yield. Yet it is certain that resistance to disease influenced the early plant-breeders, for the cropping power of the plant will depend on its ability to reach a mature state in spite of the diseases which beset it.

The fact that the resistant variety is capable of producing resistant seed was early recognized. Definite proof was established by Biffen (1), who showed that the degree of susceptibility of cereals towards Yellow Rust (*Puccinia glumarum* Erikss.) is a property which follows the Mendelian laws of heredity.

In nature the progress of natural selection is retarded by certain influences which man has been able to modify or control. The trend of natural selection is towards the production of a plant possessing the highest average resistance. The aim of the experimenter is usually to breed a variety resistant to but one or two diseases or pests, which, because of the artificial manner of cultivation of the plant, have become of exceptional severity. Under natural conditions this degree of severity of attack by any particular plant enemy will, as it is dependent upon variable factors such as the weather, itself vary from year to year. The motive force, as it were, which brings about natural selection is therefore variant in character. Man is able to keep this influence at its strongest point by maintaining continually an infestation which by artificial means is made more severe than would occur naturally. Finally, in the case of those plants which cross-fertilize, there is in nature the danger that

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the resistant form may be fertilized by a susceptible form resulting in a weakening of the inherited resistance of the seed. By controlling the fertilization of the selected variety, man is able to prevent this dilution and to " fix " the resistant variety.

There are thus two ways of approach to the production of resistant varieties—selection and hybridization.

Selection. The way of selection is the simpler and involves merely the reservation for succeeding crops of those plants which show some degree of resistance. It is thus necessary to have for the successful carrying-out of this method a thorough infestation and an indication of resistance on the part of the host plant.

An example of the successful production of resistant varieties by selection is afforded by the work of the Empire Cotton Growing Corporation Station at Barberton in South Africa. The cultivation of cotton in South Africa had been severely handicapped by the uncontrollable attack of the Cotton Jassid *Empoasca facialis* Jac. Following the observation that certain strains of American Upland Cotton (*Gossypium hirsutum*) and the Cambodia variety resisted the jassid attack (2), a comprehensive programme of selection was initiated to discover strains possessing both resistance and the desirable qualities of good staple and high yield. Worrall (3) observed that resistance was accompanied by hairiness, but as hairiness is associated in most cases with short staple, he advised that only hairy plants of good staple be used for selection. The outcome of the work has been the introduction of several strains, one of which, U4, has proved so successful that its cultivation has now extended far beyond the area for which it was originally produced.

The method of selection is too empirical to be attractive from the scientific point of view and, following the rediscovery of Mendel's Laws by Bateson and the proof, by Biffen, that the inheritance of resistance follows these principles, the method of cross-breeding or hybridization has been developed along scientific lines.

Hybridization. The study of the manner in which the qualities of the parents are inherited by the offspring has revealed that the agents carrying each specific quality are the chromosomes. At cell division, each chromosome splits into two, one half going to each cell, thus maintaining constant the chromosome complement of each cell. At germ cell formation, however, another type of division occurs in which the chromosomes are segregated and recombined, each germ cell containing but half the number of chromosomes (i.e.

is haploid). At fertilization, which involves the union of two germ cells, one from each parent, the number of chromosomes is restored to the normal (diploid) complement. By fertilization, therefore, half the hereditary characters of each parent are combined in the offspring and will become manifest or will rest dormant to reappear in subsequent generations accordingly as the character is dominant or recessive.

The phenomenon of dominant and recessive characters may be explained by supposing that each hereditable character is governed by two units or genes carried by the chromosomes. Thus resistance may be regarded as the resultant of the action of a particular gene (or genes) R, which is accompanied by an alternative gene r. The combination Rr continues through normal cell division but, at the formation of the germ cells, the units are separated, R and r going to different germ cells. At fertilization, however, the units reunite and, following the chance mating of the germ cells at self-fertilization, new individuals will appear in which the combinations RR, Rr and rr occur in the numerical ratio of $1 : 2 : 1$. Now it may be that the Rr combination will show characters intermediate to the RR and rr combinations, i.e., indifferent resistance, or that it will show only the RR character. In the latter case R is said to be dominant, r being recessive.

If R is dominant, self-fertilization of the Rr individual will give rise to offspring of which three-quarters will be resistant and one-quarter non-resistant. Self-fertilization of the RR individual can, on the other hand, produce only RR offspring. By systematic self-fertilization it is thus possible to produce offspring that breed true to type or, as expressed above, to fix the variety.

By hybridization, which is the mating of germ cells containing unlike genes, it is possible to combine the qualities of the parents. In practice, however, it is found that, in most cases, plants do not behave in the simple way outlined above. Cytological studies have now supplied an explanation of the many disappointments of early plant breeding, for they have shown that the majority of cultivated plants are not simple diploids but are polyploids in which the genes governing any character are repeated several times over. Among the plums, for example, the Myrobolan Plum (*Prunus cerasifera*) is diploid (16 chromosomes), the Sloe (*P. spinosa*) is tetraploid, the Damson (*P. insititia*) and European Plum (*P. domestica*) are hexaploid. The genetic analysis of polyploid species may be highly complex but, as the general principles summarized above for the

hypothetical R*r* parents hold, it is evident that by such an analysis, the geneticist and cytologist can discover the possibilities and limitations of hybridization.

One limitation, already well known in practice, is the production of non-fertile progeny by hybridization. The explanation of this phenomenon may be illustrated by the plum species mentioned above. Crane and Lawrence (4) found that crosses of *P. domestica* and *P. insititia* produced good seed but that crosses of *P. domestica* and *P. cerasifera* did not. In the fertile cross both parents are hexaploid but in the infertile cross one parent is diploid, the other hexaploid ; the offspring have therefore an unbalanced chromosome complement. For the same reason, the triploid varieties of plum are of use solely as ornamental plants where sterility may be an asset.

There are, however, innumerable varieties of plants which are sterile by reason of an unbalanced chromosome complement yet which are of the greatest practical value. Many varieties of apple, for instance, have been shown to be partly tetraploid and partly hexaploid and others partly hexaploid and partly nonaploid (5). Breeding trials have shown that the latter type are highly sterile and that crosses in which this type is one of the parents make feeble growth. Limitations of this character are, fortunately, of significance mainly to the plant breeder, for the desired variety may often be propagated through vegetative or asexual structures such as grafts and cuttings.

An example of the production of resistant varieties by hybridization is the work now being carried out in Germany upon the production of grape vines resistant to *Phylloxera* and *Peronospora*. Certain American species of vines such as *Vitis rupestris* are highly resistant to both of these parasites, but their fruit is of poor quality. Varieties of the European species, *V. vinifera*, though yielding fruit of high quality, are highly susceptible to these parasites. Early attempts to combine the resistance of *V. rupestris* with the fruit qualities of *V. vinifera* were not successful, for the hybrids were all of poor flavour. Genetical studies (6) have now provided a rational basis for hybridization. In Germany, from five to ten millions of hybrid seedlings have been artificially infected with *Peronospora*. The resistant seedlings were grown on and their fruit qualities determined, those satisfactory then being tested for resistance to *Phylloxera*. Baur (7) estimated that, by the middle of the present century, the required varieties would be found and the need for

combating these two pests, which at present costs the German grape-growing industry · between thirty and fifty million marks annually, would disappear.

When selecting resistant strains it is obviously advantageous to maintain the chance of infestation at the maximum and to obtain an indication of susceptibility as early as possible in the life of the plant. Hence it is customary to inoculate artificially seedlings grown under greenhouse conditions. Such a procedure may, in some cases, give misleading results. Thus Harrington (8) found that the results of greenhouse tests of the resistance of wheat seed-lings to Stem Rust (*Puccinia graminis* Pers.) were not in agreement with those obtained in the field. Goulden, Neatby and Welsh (9) further showed that mature plant resistance to this disease was independent of greenhouse resistance and could only be detected after the plant had passed a certain stage of maturity.

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THE USE OF RESISTANT VARIETIES

The use of resistant varieties was suggested as far back as 1815 by Thomas Andrew Knight (10), who advocated the cultivation of those varieties of cereals which appeared to be immune from attack by parasitic fungi.

Considered as a method of control of parasitic diseases and pests, the use of a resistant variety possesses the obvious advan-tage that it dispenses with the need of other protective measures. Once resistant varieties of equal cropping power, both in quality and quantity, are produced, the annual tax imposed on the grower by other methods of control becomes nil. From this point of view it is the most economical of the measures available against plant parasites.

The method has met with marked success in every type of crop production, but perhaps more especially in cereal growing and in

horticulture (11). The advent of resistant varieties has, in a number of instances, saved a threatened· crop. Thus, the Wart Disease of Potato (*Synchytrium endobioticum* (Schilb.) Perc.) seemed an insoluble problem to the applied mycologist until Gough observed that certain strains were unaffected by the disease. The discovery of the cucumber Butcher's Disease Resister, immune from Leaf Spot (*Cercospora melonis* Cooke), has been a major factor in the disappearance of this disease from Great Britain. It is no exaggeration to claim that the sugar-cane industry of Java could not have survived the competition of sugar-beet and the serious losses caused by the " Sereh " disease but for the discovery of resistant strains. Wild varieties of sugar-cane were found which were immune to this disease and to Mosaic, another type of virus disease, and by systematic crossing with cultivated varieties, strains were evolved which have enabled the industry to survive (12, 13).

One interesting method of utilizing this principle is by grafting, which is of special value in fruit culture where the production of resistant varieties is made difficult by the slow growth of the trees and, as mentioned above, by the complicated nature of the chromosome complement. The failure of early attempts to produce grape vines resistant to *Phylloxera* by hybridization was countered by the grafting of the European varieties on American root stocks, whereby the severe injury which the insect causes to the roots was prevented. In the eastern states of the United States, Collar Blight of apple, due to *Bacillus amylovorus* (Burr.) Trev., is avoided by topworking the desired variety on a resistant stock in such a manner that the collar and trunk of the tree will not take the disease (14). The pear is, however, even more susceptible to this disease and a resistant pear stock has now been found. Certain Asiatic species of pear, notably *Pyrus ussuriensis*, of which the fruit is of no commercial value, have been shown by Reimer (15) to be resistant. Difficulty was experienced in that this variety intergrafted poorly with the common pear, *P. communis*, but by the use of an intermediate scion it has been found possible to graft the desired pear on the resistant stock.

Unfortunately, as a method for the control of plant parasites, the use of resistant varieties suffers from severe disadvantages. Cases of good cropping varieties possessing resistance to more than one disease are rare ; a fact due no doubt to the infancy of the science of plant breeding. Further, a variety proved resistant to one strain of a pathogenic organism may be susceptible to a second

strain of the same organism.   It is now well established that there
exist varieties of many of the lower organisms which, although not
readily distinguishable morphologically, differ widely in their
physiological properties, such as their ability to establish parasitism.
To strains of organism showing such differences the terms " physio-
logic forms," " biologic forms " or " species " have been applied.
This phenomenon, first observed among the plant pathogenic fungi
by Schroeter (16), is shown most strikingly by highly specialized
fungi such as the Rusts (Uredineæ) and the Powdery Mildews
(Erysiphaceæ).   Eriksson (17), for example, established the exist-
ence of at least three biologic forms of Stem Rust (*Puccinia graminis*)
one, f.sp. *secalis* attacking rye, barley and a few grasses ; a second,
f.sp. *tritici*, attacking wheat but rarely found on other cereals ; a
third, f.sp. *avenæ*, attacking oats and a number of grasses.   Stakman
and his colleagues (18) in the United States and Goulden and his
co-workers (19) in Canada have now defined over one hundred
strains of this organism.   The infective capacity of these strains
is limited, but few varieties of wheat have been found completely
resistant to Stem Rust in all its manifestations.

The phenomenon of biologic forms complicates to an alarming
extent the difficulties of the plant breeder, but the problem, in the
case of rust resistance in cereals, appears to be slowly yielding to
the attacks of the American workers mentioned above.   The only
wheats exhibiting resistance to most of the known forms of Stem
Rust are of the emmer group and there is hope of the production,
from the emmer group, of a strain having the factor of resistance
to all known biologic forms of the rust.

The existence of biologic forms explains why varieties of crop
plant resistant in one locality have been found susceptible in another
region.   Thus the Marquis variety of wheat is considered susceptible
to Black Rust in the upper Mississippi valley yet it is free from
rust in certain regions west of the Rockies.   The Australian rust-
resistant wheat " Bobs " when introduced into South Africa (20) lost
its resistance when grown on low-lying ground, although at Pretoria
it remained immune from Black Rust (*Puccinia graminis*) ; similarly
the Australian rust-resistant wheats became freely rusted when
tried out in India.   A wilt-resistant water melon " Conqueror "
lost its resistant qualities when transferred from the Atlantic coast
of the United States to the Pacific coast (21).   Cunningham (22)
recorded the case of the apple variety " Yates," which is highly
resistant to Scab (*Venturia inæqualis* (Cooke) Wint.) in the Otago

district of New Zealand, yet may be highly susceptible in the Nelson district.

The maintenance of resistance by the host plant is thus dependent upon the non-appearance of biologic forms of new infective capacity. It was suggested by Ward (23) that the pathogenicity of a fungus can be modified by gradual adaptation to resistant hosts or by the phenomenon of "bridging species." Stakman (24) concluded, however, that the evidence for adaptation by such means in the case of rusts is inadequate. It would seem that there is little fear of the failure of a resistant variety through modification of the pathogenicity of the fungus by adaptation. But if new biologic forms of the highly specialized fungi can arise through hybridization (see p. 335), the position of the resistant host looks insecure.

In less specialized fungi such as the Fusaria or *Botrytis cinerea* Pers. there is evidence of erratic and uncontrollable variations in biologic properties (25, 26), evidence which would seem to reduce the trustworthiness of varieties found resistant to such fungi.

Similarly, among insect pests there are instances of the sudden appearance of races of insect adapted to new food plants not previously attacked. The Capsid Bug *Plesiocoris rugicollis* Fall. was not known to attack apple prior to 1900 but preferred willow. Since that time, however, a race of the bug has developed which rapidly became a serious apple pest (27).

Finally, it would seem that examples of absolute resistance are few. Resistance and susceptibility are the resultants of the interplay of many factors involving both host plant and parasite and, in the great majority of cases, these factors are influenced by environmental conditions. A consideration of the nature of plant resistance will show that in cases of non-absolute resistance, the employment of resistant varieties and the selection of environmental conditions favouring resistance is perhaps a more practical principle of plant protection.

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THE NATURE OF PLANT RESISTANCE

The problem of the nature of plant resistance, which involves not only the means whereby the plant repels parasitic attack but also the question of how the parasite makes its attack, is an immense field which has attracted much attention in recent years. It is impossible to examine the problem in detail in a single section, but it is desirable to deal briefly with the work already carried out, for it appears that in the practical application of knowledge of plant resistance lies one of the most promising fields of future work on plant protection. A sound knowledge of the factors conferring immunity or resistance and of the conditions which influence these factors is the only basis for this work.

Although the two appear to be closely related from the standpoint of plant resistance it will be better to separate, for the purpose of this discussion, the relationships of the plant to fungi from those of plant to insect.

Plant Resistance against Fungi.

The majority of parasitic fungi live within the plant tissue and are known as " endophytes," in contradistinction to those which live on the surface of the plant. This latter class—the " ectophytes "—may be subdivided into the pure ectophytes, which live in close union with the outer surface of the plant, and those which develop haustoria serving as organs whereby the mycelium of the fungus, which remains outside the plant tissue, derives its food.

Infection is generally the result of two processes, firstly the penetration of the germ tube of the spore into the plant tissue, secondly the establishment of the fungus growth in or on the host— the infection proper. The successful accomplishment of the first

stage will only result when the fungal spore is able to remain in
contact with the host tissue and when it experiences the conditions
necessary for its germination.   It is possible that the waxy surface
of certain leaves and fruit-skins may render that plant resistant
by permitting the water to flow off rapidly, this preventing the
accumulation of water which is necessary for the germination of
the spore.   Those varieties of raspberry which are least damaged
by the rot caused by *Coniothyrium* spp. possess a more waxy surface.
Again, potatoes with small hairy leaves and an open habit of growth
permitting the leaf surface to dry rapidly after wetting appear less
liable to infection by Blight (*Phytophthora infestans* (Mont.) de
Bary).

In many cases it has been established that the germination of
fungus spores is stimulated by the presence of plant tissue.   Brown
(28) first showed that the vigour of germination of spores in the
infection drop is influenced by the exosmosis of material, which he
assumed to be food substances, from the host tissue.   Durrell (29)
demonstrated that stimulation was not obtained in the presence of
barium hydroxide and therefore concluded that the active agent
was carbon dioxide, a conclusion confirmed by Platz, Durrell and
Howe (30).

Penetration.   If conditions are favourable to the germination of
the fungal spore, it will proceed with the process of penetration.
The first stage of penetration may occur by direct passage through
the wall of the epidermis or via the stomatal pore.

In the simpler case—penetration by way of the stomata—it must
be assumed that the growth of the germ tube from the spore towards
the stomata is induced by some physical or chemical stimulus.
Possibly this stimulus is due to the greater moisture content of the
air in the stomatal cavity and is therefore an example of positive
hydrotropism.*   In other cases it may be that stomatal penetration
is due to the diffusion of some volatile chemical through the stomata,
for Neger (31) showed that volatile chemicals can influence the
germination of fungus spores.   Arens (32) demonstrated that in
the case of certain fungi which exhibit zoospore formation, the
movement of the zoospores is influenced by the attractant properties

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* The direction of growth or movement of an organism is, at times, controlled
by external influences such as light, gravitation, heat, chemical influences,
etc.   According to the nature of the controlling influence this phenomenon, a
tropic response, is known as phototropism, geotropism, etc., positive or
negative according as the direction is towards or away from the source of the
stimulus.

of substances, presumed to be phosphatides, exuded from the stomata.   Upon leaves giving no phosphatide reactions, he found that the zoospores did not collect at the stomata.   The directional growth of the germ tube and movement of the zoospores are examples of positive chemotropism.

Immunity will result if this stimulus is lacking or if the penetration of the germ tube into the stomata is mechanically prevented. The susceptibility of sugar-beet towards Leaf Spot (*Cercospora beticola* Sacc.) has been considered to be dependent, among other factors, upon the length of the stomatal pore (33).   Doran (34) demonstrated that the resistance of snapdragons to *Puccinia antirrhini* is conditioned by the number of stomata per unit area. Resistance of stone fruit to *Sclerotinia cinerea* (= *S. laxa* Aderh. & Ruhl.) was considered by Curtis (35) to be determined by the toughness of the cuticle and the size of the stomata.

Further, the growth of the germ tube towards the stomata may be hindered, for example, by the presence of hairs on the leaf surface.   The young leaves of the grape vine are not attacked by Black Rot (*Guignardia bidwellii* (Ellis) V. & R.), partly owing to their dense covering of hairs, while Apple Scab (*Venturia inæqualis*) is less common in the under-surface of the leaves, perhaps because of their hairy nature.   Hursh (36) concluded that stomatal movements may have some influence on the entrance of the germ tube of Black Rust (*Puccinia graminis*) of wheat and showed that these movements are affected differently in different varieties by the environmental conditions.

The entry of the fungal germ tube into the host by direct penetration through the outer wall of the epidermis appears to result from a more complex series of reactions on the part of both parasite and host.   Not only has the direction of growth of the germ tube to be controlled but the germ tube is required to force its way through the epidermal layer of the plant tissue.

Various mechanisms have been suggested which may contribute to the control of the directional growth of the germ tube.   It is possible that the mere contact of the spore with the solid substratum supplies the necessary stimulus—that the direction of growth is an example of stereotropism (thigmotropism or haptotropism).   On the other hand, the direction of growth may be determined by movement from light—an example of negative phototropism.   Miyoshi (37) developed the idea that the fungus, responding to nutrient material diffusing from the host tissue,

grows towards the source of this nutrient, an example of chemo-
tropism. His hypothesis has been criticized by Fulton (38), who
suggested that the directional growth is due to the tendency of the
fungus to grow away from its own waste products—a negative
chemotropism. Graves (39) found support for both hypotheses
but concluded that negative chemotropism was the more important.

In these few cases, the germination and growth of the spore will
be independent of the host plant and entirely non-specific. But
if positive chemotropism is involved, specificity may be introduced
if susceptible varieties possess, in their cells, attractive substances
absent from resistant plants. This idea was elaborated by Massee
(40), but it has received little support from subsequent work.
Brown and Harvey (41) showed that penetration of epidermal
tissue and of artificial membranes can be achieved by *Botrytis
cinerea* in the absence of chemotropic stimulus and they suggest
that, until found inadequate, the hypothesis of a contact stimulus
provides a satisfactory explanation.

The force necessary to effect the penetration may be supplied by
the energy of growth of the germ tube, or it may be that the fungus
secretes an enzyme-like substance which aids the penetration of
the germ tube by dissolving or by softening the cell wall. Miyoshi,
(37) favouring the mechanical method, considered that the resistance
necessary for the exertion of pressure by the germ tube is supplied
by the physical adhesion of the spore to the plant surface. The
researches of Blackman, Brown and their co-workers (42) have
shown no evidence of the existence of enzymatic activity in this
penetration. No enzyme is known capable of dissolving or of
softening the plant cuticle, and the existence of brown coal, which
consists largely of cuticular plant material, is evidence of the
resistance of the cuticle to enzymatic decomposition. The mech-
anical hypothesis seems more feasible and much work has been
carried out on the correlation of disease resistance and the mechanical
resistance of the cell wall. De Bary (43) regarded the turgidity of
the cell membrane as a decisive factor, and it has been shown that
the fungus makes an easier entry into leaves rendered flaccid by
chloroforming or by wilting. The waxy leaf and fruit coverings
may also asist in hindering the penetration of the germ tube just as,
as has been mentioned above, they rendered conditions unfavourable
for the germination of the fungal spore. The comparative resist-
ance of the fruit of certain plum varieties to Brown Rot (*Sclerotinia
cinerea*) has been attributed to the toughness of their skin and the

firmness of their flesh (44). Willaman (45) by the measurement of these two factors, adduced evidence to show that the " skin test " alone is a sufficient criterion for the determination of the degree of resistance of plum varieties to this fungus.

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Establishment of Infection. Establishment of infection will result after successful penetration of the germ tube when the conditions within the host are suitable. The spore may germinate and invade the tissue even of a resistant host, but establishment of the infection then fails and the fungus dies off. Thus Marryat (46) showed that the hyphæ of Yellow Rust (*Puccinia glumarum*) will penetrate the stomata of resistant wheats but that further progress of the fungus is prevented by some unfavourable condition within the host.

Cytological studies, which are well exemplified by the work of Allen (47), have established that with highly specialized fungi such as the Rusts, establishment of infection fails through the rapid death of host tissue at the seat of infection. Resistance in such cases is due to the high susceptibility (hypersensitiveness) of the host plant. The fungus, after expending its food reserves in penetration, is unable to derive nutriment from the barrier of dead host cells.

In other cases the extension of fungal invasion may be prevented by various mechanical, chemical and physiological factors. An example of mechanical resistance is afforded by Hawkins and Harvey

(48), who indicated that the degree of attack of potato by *Pythium de Baryanum* Hesse is limited by the thickness of the cuticle.   The resistance of wheat seedlings to *Gibberella saubinetii* (Mont.) Sacc. was correlated by Dickson, Erkerson and Link (49) with the pectin content of the cell wall.   Alternatively, the host plant may be able to protect itself from the extension of fungal invasion by morphological changes induced by the attack.   Thus it is supposed that the formation of a cork layer in potatoes attacked by either Corky Scab (*Spongospora subterranæ* (Wallr.) John.) or Common Brown Scab (*Actinomyces scabies* (Thax.) Güssow) (50) is an attempt to isolate the infected tissue.   Appel and Schuster (51) showed that the varieties of potato resistant to rotting bacteria are those which after twenty-four hours have formed a connected cork tissue across a cut surface.   Tisdale (52) found that varieties of flax resistant to Wilt (*Fusarium lini* Bolley) developed a layer of suberized cells in advance of the penetrating fungal hyphæ, which effectively walled off the parasite.   Brooks and Moore (53) mentioned plum varieties (e.g. Pershore) resistant to Silver Leaf (*Stereum purpureum* Pers.) because of their ability to produce quantities of gum which forms a barrier preventing extension of fungal growth.

The rapid isolation of the infected tissue also plays an important part in the protection of the plant against facultative parasites. This type of parasite penetrates the dead tissue first as a saprophyte and after securing infection is then able to attack the living plant cells.   The formation of tannin-like material by apples and other ,fruits after wounding retards the growth of such parasites.   The secretion of latex, gum or wax often acts as a protective against wound infection.

Of the chemical factors, the suggestion of Comes (54), that the acidity of the cell sap determines resistance, has provoked much research.   Arrhenius (55) could establish no correlation between the hydrogen ion concentration (i.e. the intensity of the acidity) of the cell sap of wheat plants and resistance to Yellow Rust (*Puccinia glumarum*) ; but he considered that the titratable acidity (i.e., the quantity of acid) of the *living* cell sap might have some influence. He showed, however, that the titratable acidity of the cell sap pressed out of the plant gave no such relationship.   Hurd (56) showed that the varietal resistance of wheat to the Stem Rust (*Puccinia graminis*) is not related, at any stage of development of the host, to the titratable acidity, or to the hydrogen ion concentration of the cell sap.   He found that the hydrogen ion con-

centration of the cell sap varies throughout growth and that the resistant varieties of wheat pass through the period of low concentration at the same stage of growth as do the susceptible varieties, yet no breakdown in their resistance at this stage could be detected.

On the other hand, cases of the correlation of the acidity of the cell sap and the plant's degree of resistance have been reported. Molz (57) reported that those varieties of vine resistant to Mildew have leaves whose sap acidity is 4·3–10·3 per cent. (expressed as tartaric acid and calculated on the dry matter), whereas the more susceptible varieties have but 0·5–2·6 per cent. acidity. Gardner and Kendrick (58), found that in the disease of tomato due to *Bacterium exitiosum* Gard., inoculation of the ripe fruit frequently failed, whereas the young seedlings could be readily infected. They traced this failure to the higher hydrogen ion concentration of the sap of the mature plant, to which they attributed its resistance to infection. It is reported that, in the case of the Black Rot of Grapes (*Guignardia bidwellii*), the more susceptible varieties are richer in acids and form sugars late, whereas the more resistant varieties have little acid and become rich in sugars early in life. The influence of sugar on the growth of the fungus after penetration was also pointed out by Tischler (59), who, in his work upon the infection of *Euphorbia cyparissias* by *Uromyces pisi* Wint., found that the extension of the mycelial growth seemed to be dependent on the sugar content of the plant tissue.

The ability of the fungus to thrive after penetration will depend on the presence of the required food material in the plant tissue. It is well established that some fungi are extremely sensitive in this respect. Pasteur (60), in 1860, utilized this " specificity " of *Penicillium glaucum* Link. for the separation of the optically active isomers of tartaric acid.* The fungus, on addition to a mixture of derivatives of these two acids, is able to utilize as food the deriva-

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* Tartaric acid is known in four forms, identical in composition and differing only in the arrangement of the relative positions of the groups of atoms within the molecule. Two of these forms are optically active ; they have, in solution, the power of rotating the plane of polarized light, the one being dextro-rotatory, the other lævo-rotatory, and are represented by the following formulæ :

$$
\begin{array}{cc}
\text{COOH} & \text{COOH} \\
| & | \\
\text{HO—C—H} & \text{H—C—OH} \\
| & | \\
\text{H—C—OH} & \text{HO—C—H} \\
| & | \\
\text{COOH} & \text{COOH}
\end{array}
$$
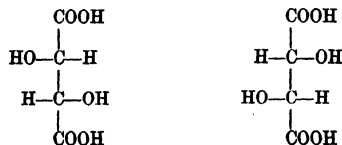
tives of one only. It has since been shown (61) that the fungus is able to use both compounds as food, but that it attacks derivatives of the dextro-isomer with far greater rapidity than it does the lævo-form. Many examples of this high specialization in the type of food required are now known among the bacteria and fungi, and Leach (62) has suggested that such specificity of food requirements on the part of the parasite and a similar specificity of food production on the part of the host plant may prove causes of disease resistance.

A hypothesis, similar in certain respects, has been put forward by Coons and Klotz (63), who considered that the ability of an organism to thrive in the tissue of a plant will be dependent upon its ability to attack the food substance, especially the protein, of the host. The breaking down of the protein is accomplished by certain enzymes, which may be furnished by the fungus itself, or which may arise from the host plant as a result of the invasion of its tissue. The rôle of the enzyme pectinase, which assists in the breakdown of pectin, in determining the parasitizing ability of *Botrytis cinerea* has been examined by Brown and his co-workers (64) whose results have shown the enzyme hypothesis to be of great usefulness in interpreting the behaviour of non-specialized parasites of this type. For example, Vasudeva (65) was able to show that the fact that the fungus *Botrytis allii* Munn which is normally non-parasitic on apples (in storage), but which produces definite attack if supplied with a small quantity of nitrogenous nutrient, is associated with the ability of the fungus to excrete pectinase when supplied with nitrogenous food. In the same way, Horne's (66) observation, that there is a high degree of correlation between the nitrogen content of different apples of the same variety and the rate of invasion by parasitic fungi, may be explained by the intensifying influence of the nitrogen status upon the secretion, by the fungus, of pectinase.

It may be that there are present in the plant, prior to penetration, certain materials toxic to the invading fungus. Angell, Walker and Link (67), for example, found protocatechuic acid in the outer scales of onions resistant to the Onion Smudge *Colletotrichum circinans* (Berk.) Vogl. Newton and Anderson (68) obtained evidence that phenolic substances determine the resistance of wheat to Rust, whilst Dufrénoy and his colleagues (69) showed, by micro-precipitation methods, that phenolic compounds are formed in the host plant cells adjacent to infected cells. Thus he demonstrated that the cells of bean plants resistant to *Colletotrichum lindemuthianum* (Sacc. and Magn.) Bri. and Cav. developed tannin vacuoles, whereas

infected cells of susceptible plants became crowded with starch grains.

The precise rôle of tannin and related phenolic compounds in plant metabolism has been widely debated (70), and it is not impossible that they serve for defence. Cook and Taubenhaus (71) suggested that the greater susceptibility of mature over immature fruit to fruit rots is associated with the smaller content of oxidase in the mature fruit. The oxidase, they considered, served to protect the infected fruit by the liberation, from the tannin, of phenolic derivatives toxic to the invading fungus.

Alternatively, certain glucosides have been considered to be the active means of defence of resistant varieties. Tims (72) suggested that the resistance of cabbage to Cabbage Yellows (*Fusarium conglutinans* Wr.) is due to a toxic principle, possibly a sulphur-containing glucoside, present in the tissues of resistant plants. Reynolds (73) recognized two types of substance present in flax extracts and toxic to *Fusarium lini*, the organism responsible for Flax Wilt : firstly, the glucoside linamarine, which appeared to be present in higher amount in resistant strains of flax ; secondly, toxic substances, stable to heat, which appear to vary in amount according to environmental factors and to the strain of flax.

The production of toxic substances from the reaction of host plant and fungus is a commonly accepted explanation of the wilting caused by certain Fusaria. White (74) reviewed the evidence which suggested that two toxic principles are involved, one, enzymic and thermolabile, the second, crystalline and thermostable. Resistance may thus be due to the presence of substances capable of rendering non-toxic to the host plant the toxins arising from fungus attack.

The suggestion that some specific chemical substance toxic to the fungus is formed by the interaction of host plant and fungus has been subjected to experimental trial. Roach (75) by an ingenious technique involving the grafting of the root, shoot and tuber systems of varieties of potato susceptible and resistant to Wart Disease (*Synchytrium endobioticum*) showed that the " cause " of immunity is not a substance produced in one part of the plant, and translocated thence to other parts of the plant. Nor was evidence of the interchange of the " cause " of resistance across grafts obtained by Leach (76) in beans resistant and susceptible to *Colletotrichum lindemuthianum*, by May (77) examining the response of tomatoes to *Fusarium lycopersici* Sacc., or by Salmon and Ware (78) working with hops resistant and susceptible to *Sphærotheca*

humuli (DC.) Burr. It would appear that, in these cases, the substance to which resistance in susceptibility is due does not leave the cell and that it is inseparably connected with the protoplasm, or possibly with the proteins which are invariably constituents of protoplasm. Roach suggested that, in view of the specificity of the proteins shown in immuno-chemical reactions, the most hopeful line of attack in the determination of the cause of immunity is an examination of the proteins of immune and susceptible varieties by immuno-chemical methods.

That, however, the scion may, in some cases, have an influence upon the susceptibility of the stock is shown by an example quoted from Wormald and Grubb (79). These workers found that the susceptibility of the apple stock to Crown Gall (*Bacterium tumefaciens* E. F. Sm. & Towns.) is modified by the variety of the scion grafted on it. Lord Derby rendered the stock more susceptible, whereas Bramley's Seedling scions appeared to increase the resistance of the stock to this disease.

The suggestion that the factor determining resistance may prove to be related to the specificity of the proteins of the plant tissue has been examined by Nelson and Dworak (80) in flax plants resistant to Wilt (*Fusarium lini*). They separated the globulins from the seed of a resistant and of a susceptible variety into two fractions, both of which were proved to possess a high specificity by precipitin tests. These workers concluded that their trials indicated, though did not prove, that the globulins from the resistant variety possessed a serological peculiarity which is absent from those extracted from susceptible seed. Resistance to Wilt may then be associated with the globulin fraction, though whether it is a result of the globulin structure or whether it is due to some factor connected with the globulin vehicle, they were unable to determine.

The possibility that immuno-chemistry is concerned in disease resistance in plants has resulted in speculations on the feasibility of utilizing, for plant protection, the immunological methods employed in animal pathology. These methods mainly depend on the principle that the animal responds to the introduction, within its body, of an antigen by the formation of an antibody which reacts specifically with the antigen. By injecting the antibody or by stimulating its production within the animal, that animal acquires resistance to the corresponding antigen or to the organism producing that antigen. The ability of fungal and bacterial pathogens

to produce antibodies in the animal body is proved. Coons and his co-workers (81) employed methods dependent on antibody formation, e.g. the complement fixation test, the precipitin and agglutinin tests, to differentiate between strains of Fusaria ; Edgecombe (82) adapted a precipitin test to distinguish varieties of wheat of varying resistance to rust ; Link *et al.* (83) correlated the serological specificity of certain phytopathogenic fungi with their biological specificity. If these pathogens can induce antibody formation in the plant, the plant may acquire resistance to that pathogen. The first attempt to prove antibody formation in the plant was due to Potter (84) who isolated, from turnips infected with White Rot (*Bacterium carotovorum* (L. R. Jones) Lehm.), a substance which prevented the growth of this bacterium on inoculated turnip. Mallmann and Hemstreet (85) were able to isolate an inhibiting substance from a rotten cabbage which was active against an organism obtained from the same cabbage. Sardiña (86) was unsuccessful in his attempts to isolate specific agglutinins and precipitins from plants inoculated with certain phytopathogenic bacteria. But the difficulty of proving antibody formation may hinge on the possibility, indicated from the results of the grafting technique described above, that the antibody, the " cause " of resistance, cannot leave the plant cell in which it is formed. In the animal, the blood circulatory system provides a channel for antibody translocation but, in plants, it would seem that immunological phenomena must be largely if not entirely cellular. Chester (87), who has provided a general survey of plant serology, advanced arguments against this distinction between zoo- and phyto-immunology, but it is maintained by Butler and by Salaman (88).

Although partial success has been claimed by Carbone and his colleagues (89) in the immunization of plants, it is but recently that cases of acquired immunity have been established. Wingard (90) found that many different varieties of host plant, when infected with Tobacco Ringspot virus, develop symptoms of infection, but that after about two weeks the new growth shows but faint symptoms, until finally normal growth is obtained. Reinoculation of the recovered plants or of cuttings taken from such plants failed though the sap from these plants induced the disease, showing that the virus was still present. The treated plants thus acquire tolerance to the virus but have become " carriers " (see p. 330). The second type of acquired immunity was first reported, in 1931, by Thung (91). He observed that tobacco plants suffering from

Tobacco Mosaic failed to develop symptoms of a " white mosaic "
when inoculated with this virus.   The practical significance of this
discovery was developed mainly by Salaman (92) who suggested
that, by infecting a plant with a mild strain of a particular virus
causing minor loss of cropping value, the plant can be protected
against more virulent strains of the same virus.   As protection is
not necessarily obtained against other viruses, the phenomenon
exhibits a specificity comparable to that of acquired immunity in
animal pathology, but it seems doubtful whether this specificity is
due to analogous serological causes.   Bawden (93) suggested that
there may be a maximum amount of any virus that a plant can
contain and if one strain has already grown to this amount a second
is unable to multiply.   As a plant fully infected with one virus is
still susceptible to other unrelated viruses, it seems that related
viruses either occupy the same sites or utilize the same materials
whereas unrelated viruses multiply at different sites or use different
materials.   The difficulties of the practical application of this type
of vaccination for plant protection purposes are discussed by
Henderson Smith (94).

Such is a brief review of some of the many factors which may
contribute towards the resistance of plants to fungus attack.   The
entry of the fungus may be prevented by the inability of the spore
to find those conditions necessary for its germination ; the stimulus
necessary to secure penetration may be lacking ; the penetration
of the germ tube may be prevented by the morphological character
of the host ; the establishment of infection may be prevented by
unsuitable conditions within the host such as hypersensitiveness,
factors preventing enzymic activity, the presence of specific chemical
substances toxic to the fungus ; the development of the fungus may
be inhibited by a defensive response of the host plant which may
involve morphological changes or the production of specific toxins.

Finally, it is evident that it is most improbable that any single
explanation of plant resistance can be adopted as a generalization
covering all types of host-parasite relationship.   The nature of
plant resistance is clearly complicated and the hypotheses so far
advanced are, in general, sufficiently elastic to permit a reasonable
explanation of the profound effect which environmental conditions
frequently display in determining the degree of attack.

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Plant Resistance against Insects.

The factors contributing to the resistance of plants against fungal
and bacterial attack, examples of which have been cited in the
previous section, are not so apparent in the case of the resistance
of the host towards insect injury.   It is obvious that the conditions
necessary for the germination and subsequent growth of the fungus
spore, especially of the endophytes, are more numerous and delicate
than those which govern the extent of injury caused by insects.
The methods of attack of insects are far more varied than are
found in fungus diseases.

It is possible to classify roughly the methods by which the insect
obtains its food from the plant under two heads based on the con-
struction of the mouth parts of the insect.   Firstly, there are those
insects possessing horny jaws which chew the plant tissue ; to this
class belong the grasshoppers, beetles and caterpillars, known as
chewing or mandibulate insects.   Secondly, there are those insects
in which the mouth parts are modified to form needle-like organs
by means of which the insect pierces the outer surface of the plant
tissue and derives its nourishment by sucking the liquid cell contents.
These suctorial insects include the various scale insects and aphides.

With the suctorial insects there is a rough analogy to the fungi
in the penetration by the pest into the host tissue ; an analogy
which may be extended to include those groups of the mandibulate
insects in which the egg is deposited, by the penetration of the
ovipositor, within the plant tissue of the host.   With these latter
classes of insects, one factor to which the plant's resistance is due
is considered to be the mechanical resistance of the tissue.   Hase-
man (1) showed that the extent of infestation of three varieties of
wheat by the Hessian Fly (*Mayetiola destructor* Say) seemed to
vary with the ash content, whilst McColloch and Salmon (2) gave
indications that the varietal resistance of wheat to this pest is
associated with the presence of silica.   Moreover, with these types
of insect, more particularly the aphides, there is a rough parallel
to the more specialized nature of fungi in that the separate species
of both are tolerant to but a few species of host plant.   For example,

the apple varieties Northern Spy and Majetin are resistant to the attack of Woolly Aphis (*Eriosoma lanigerum* Hausm.), a property which Le Pelley's results (3) indicated is inherited on Mendelian lines.

Northern Spy has been widely used in the Dominions as a rootstock · because its immunity from Woolly Aphis confers freedom of roots and stems from this pest. But as it exhibits some undesirable rootstock qualities (4), a comprehensive survey is in progress at East Malling (5), of the genetical basis of this immunity in order to combine this property with better pomological qualities. At the same time the causes of immunity are being investigated, for the hypothesis suggested by the observation of Staniland (6), that resistance is associated with the completeness of the sclerenchymatous ring whereby the entry of the insect stylet into the vascular tissue is prevented, has proved inadequate. The work of Massee and Roach (7) indicates that resistance to Woolly Aphis is associated with an alcohol-insoluble but ether-soluble material present in the host tissue.* The horticultural aspects of Woolly Aphis control are discussed by Greenslade (9).

As in resistance to fungal attack, nutrient conditions within the host may determine the degree of infestation by insect pests through influence on the rate of reproduction, the rate of growth and the longevity of the pest. Resistance may also be due to the absence from the host of attractant material or of substances necessary for insect growth or to the presence in the host of repellents or toxic products. For example, Davidson (10) found that on the susceptible variety of bean, Prolific Longpod, the mean infestation figure fourteen days after the plants had been infested with a single female of *Aphis rumicis* was 1,037 ± 51·8 whereas, under the same conditions, the shoots of the more resistant winter bean bore but 286 ± 27·2 aphides.

Similarly Evans (11) was able to correlate the rate of reproduction of the aphis *Brevicoryne brassicæ* L. with the nitrogen content, in particular the protein content, of the host tissue.

The influence of attractant materials in the host tissue was first examined by Verschaffelt (12) who showed that the larvæ of the cabbage butterfly, *Pieris brassicæ* L., seek out the different mustard

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* In a later report (8) Roach modified this description to suggest that the factor responsible for the difference between resistant and susceptible varieties is insoluble both in alcohol and in ether, but the experimental data presented are incompatible with those of the earlier publication (7).

oils present in cruciferous plants. Raucourt and Trouvelot (13), in the course of their attempts to breed varieties of potato resistant to Colorado Beetle (*Leptinotarsa decemlineata* Say), an insect confined to the Solanaceæ, examined the reaction of both the larvæ and the adult beetle to the host plants. With the larvæ the attractiveness of the potato, a favoured host, was determined by certain attractive principles which, though apparently not solanin, appeared to be nitrogenous compounds.

That the presence of toxic substances may be responsible for resistance is illustrated by the suggestion of Molz (14) that the resistance of African cacao to the larvæ of *Ephestria elutella* Hb. might be due to the richness of the bark in tannin matter, which is present in but small amount in the more susceptible Guatemalan and Venezuelan varieties. Prell (15) attributed the immunity of certain pines from the attacks of the Nun Moth (*Lymantria monacha* L.) to the presence, in the needles, of about one-half per cent. of turpentine, which is absent from the needles of other pines. Similarly, Oshima (16) traced the immunity of teak and the Cypress pine from the Formosian termites to the presence of a sesquiterpene alcohol.

The protective rôle of the essential oils present in the rind of citrus fruits against the Mediterranean Fruit Fly (*Ceratitis capitata* Wied.) has been established by the work of Back and Pemberton (17). These authors have shown that, although the presence of the oil is insufficient to deter the insect from ovipositing upon the fruit, yet the female can hardly avoid puncturing one or more of the oil cells in the process. The oil so freed is an active agent in killing the eggs.

It would appear that the closely related problem of the part played by the glucosides and the alkaloids in plant economy may have an important bearing on the question of varietal resistance. Varieties of willow, for example, differ widely in the extent to which they are attacked by insect pests. Barnes (18) found that the order of resistance of certain species and hybrids to the midge *Rhabdophaga heterobia* H. Lw., causing Button Top, was inverted in the case of the sawfly *Pteronidea melanaspis*. This inverse order suggests that a chemical constituent of the leaf is concerned which is repellent to one insect but attractive to the second (19). Willow varieties were also grouped into classes severely attacked, attacked and not attacked by the beetle *Phyllodecta vitellinæ* L. by Hutchinson and Kearns (20), a classification which exhibited a degree of

correlation with the list derived by Barnes. Kearns (21) reported that a correlation had been found between the salicin content of the variety and its liability to attack by the Willow Beetle. It seems significant that salicin and the other glucosides appear mainly in those parts of the plant, namely the seed and the bark, especially liable to attack.

Finally, the extent of injury caused by the attack of the insect pest may be related to the degree of response of the plant to that attack. That there is, in many cases, a definite response by the plant, in a manner analogous to its response to the attack of certain fungi, is shown by the development of hypertrophic tissue such as in gall formation. The " Big Bud " of black currant is the result of the hypertrophic development of the bud attacked by the mite *Eriophyes ribis* Nal., and Lees (22) was able to ascribe the apparent immunity of certain varieties of black currant to an extreme susceptibility. The growing point of the attacked bud in these varieties is killed and not stimulated to the irregular growth which affords the food supply of the attacking organism, and which occurs in those varieties which show Big Bud.

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THE INFLUENCE OF EXTERNAL FACTORS ON THE SUSCEPTIBILITY AND LIABILITY OF THE PLANT TO ATTACK

The various factors which determine the resistance of the plant to both fungal and insect attack, discussed in the preceding chapter, may be classified broadly into two groups : firstly, physiological factors intimately bound up in the protoplasm of the plant; secondly, morphological factors connected with the physical and chemical properties of its tissue and sap. Although both groups contain genetic characters comparable with other hereditary factors, it is possible that such characters are capable of modification by environment. This chapter deals with the modification of the resistance of the plant by the external growth factors, and the utilization of such modifications as pest-control measures.

The problem is two-sided, for those external conditions affecting the host plant will also, directly or indirectly, affect the parasite. Not only, for example, may the temperature affect the resistance offered by a plant towards a pest, but it may influence the virulence of that pest. Indeed, in some instances the immunity of the plant is only apparent and results, not from any inherent resistance, but because the external ecological conditions are unfavourable to the pest. The possibility that the degree of attack may be reduced by the utilization of factors unfavourable to the parasite opens up a wide field of plant protection.

These factors may be divided into two groups : firstly, non-biological, such as nutritional and climatic factors, secondly, biological, such as the organisms responsible for the parasitism of the pests themselves. The employment of the biological factors restraining the increase and the virulence of the parasite is termed " Biological Control," the subject of the next chapter.

The present subject is, therefore, the utilization of the influence of non-biological ecological factors upon the extent of parasitism. As has already been indicated, this subject may be viewed from

two aspects, the effect of external factors, firstly, upon the host plant and, secondly, upon the parasite. For convenience, a differentiation will be made between these two aspects, and effects ascribable to changes in the resistance of the host will be referred to as changes in its susceptibility, whereas effects due to alterations in the numbers or virulence of the parasite will be regarded as changes in the liability of the host plant to attack.

In many cases it is impossible to make a sharp division between "susceptibility" and "liability." It has been found, for example, that excessive nitrogenous manuring "predisposes" the plant to attack, a predisposition which has been ascribed to changes in the host plant which render it more susceptible. Alternatively it has been regarded as due, not to an inherent change in the plant, but to the greater vegetative growth and delay in maturation by which infection of the plant is rendered more probable. Further, it is conceivable that the greater vegetative growth, by shading and interference with air circulation, renders the conditions around the plant more favourable to the pest.

Thus there may be a transition from extreme cases in which external factors cause a breakdown in the plant's resistance (1) to those in which the external factors ensure the absence of the pest. The arbitrary distinction of susceptibility and liability serves, however, a useful purpose even if it cannot be discerned in intermediate cases. In these cases, it is extremely difficult to demonstrate whether any change in the degree of attack induced by some modification of the growth factors is due to an effect upon the host plant, to a combination of effects predisposing the plant to attack, or to an effect upon the parasite.

The external growth factors may be classified under two heads : nutritional and climatic. The former embraces the wide field of soil conditions, fertilizer and water supply ; the latter includes temperature, humidity and rainfall.

NUTRITIONAL FACTORS

Of these factors, that which lends itself most easily to modification and, incidentally, to study, is that of the supply of fertilizers.

The Influence of Fertilizers. The observance of the profound influence of nutrient supply on the health of the plant must have followed rapidly after the pioneer work of Lawes and of Liebig on plant nutrition. Liebig (2) himself observed that on

two fields differently manured the same potato variety behaved differently towards disease. He quoted the experiments of Nagelli and Zoller on the pot culture of potatoes, who concluded that those factors which promote the normal growth of the plant are simultaneously those factors which protect it from disease.

Subsequently it has been found, as has already been mentioned, that nitrogenous manuring, especially with the more readily assimilated nitrates, creates a predisposition towards disease. Laurent (3) found that the susceptibility of potato to Blight (*Phytophthora infestans*) was increased by nitrogenous manuring ; a similar effect induced by liming he attributed to the indirect stimulation of the nitrification in the soil. Spinks (4) proved that the susceptibility of wheat grown in nutrient solution towards Mildew (*Erysiphe graminis*) and Yellow Rust (*Puccinia glumarum*) could be enhanced by supplying available nitrogen, an experimental verification of the observation of Little (5) that heavy manuring, especially with nitrogen, predisposed wheat to rust. It is now generally accepted that nitrogenous manuring leads, if not to a definite reduction in plant resistance, at least to an increased liability to disease.

In support of this view it has been found that lack of available phosphate and potash induces a decline in resistance. At Rothamsted, those plots not manured with potash are always the first to succumb to pests. The potash-starved mangold plots suffered from Leaf Spot (*Uromyces betæ* (Pers.) Tul.), whereas the surrounding plots, equally liable to infection, remained healthy. Also, it has been the usual experience that an increased mineral manuring (i.e. potassic and phosphatic manuring) renders the plant more resistant to fungal and insect pests. Stakman and Aamodt (6) reported from their experiments that, while the direct effect of fertilizers on the development of Stem Rust (*Puccinia graminis*) of wheat seems to be slight, the indirect effect is profound. By the avoidance of excessive fertilization with nitrogen and by the use of phosphatic and potassic manures they reduced the damage caused by this parasite. Gassner and Hassebrauk (7) demonstrated a clear correlation between susceptibility to rust and the mineral nutrition of the crop, a factor being the protein content of the cereal foliage.

An example of the successful use of potash is in the control of " Streak " Disease of tomato (originally called " Stripe " and attributed to *B. lathyri*). The incidence of this virus disease on

plots of the variety Comet receiving complete artificials was 40, whereas on the plots not receiving potash it was 78 per 120 plants. On 120 plants of the variety Kondine Red, 13 were diseased on the complete artificials plots but 33 on the plots from which potash had been withheld (8).

The classic example of the favourable effect of potash fertilizers in reducing insect attack is due to Andrews (9), who showed that the manuring of tea bushes so as to produce a high ratio of available potash to available phosphate in the soil, greatly reduced the infestation by the capsid *Helopeltis theivora* Waterh.

The manner in which the supply of nutrient affects the resistance of the plant is unknown. It is generally assumed that its effect on the more profound physiological factors to which the resistance of the plant may be due, is but slight. It is more probable that any alteration of the relative susceptibility of the plant is due to some modification of the morphological characters. Nitrogenous manuring induces a " soft " growth, an increased leaf area of a more succulent, sappy nature. Remer (10) ascribed the predisposition of cereals to rust attack by the action of nitrogenous manures to the greater vegetative vigour and the increase of leaf surface ; whilst Bewley (11) was of the opinion that excess of nitrogen induces a rapid-growing, soft and sappy plant susceptible to disease, ascribing the special value of potash to its " hardening " effect. In addition, the view has been advanced that any alteration of the degree of attack dependent on the manuring may not be due to direct change of the plant's resistance but to some change in its mode of growth. Gassner (12) concluded that the differences in the attack of Stem Rust (*Puccinia graminis*) on the differently manured plots are attributable not to differences of resistance dependent on the manuring but to differences in the stage of development of the plant. In spite of the different manuring of the plots, plants of the same stage of growth always showed an approximately equal development of rust. Armstrong (13) referred to the delay of maturation of wheat manured with nitrate of soda and considered that the opportunity for the development of Yellow Rust (*Puccinia glumarum*) is thereby increased ; that the effect of nitrogen is due to a lengthening of the growing period rather than to an actual increase of susceptibility. Phosphates, in general, have the reverse effect so that the plant is enabled to reach maturity before the attack of the parasite is made. Frew (14) was able to explain the relative freedom of summer barley from infection by

Gout Fly (*Chlorops tæniopus* Meig.) when manured with phosphates to the earlier development of the head. The number of leaf laminæ arising from a shoot above the level of the apex of the ear at the time of oviposition is thereby lessened and the chance of the downward-crawling larvæ, hatching from eggs on these leaves, of reaching the ear is correspondingly decreased.

Although the generalization that nitrogenous manuring predisposes the plant to fungus and insect attack and that potassic and phosphatic fertilizers have an opposite effect is on the whole true, there are notable exceptions. Bewley (11, p. 48), showed that not all diseases favour the soft growth resulting from excess of nitrogenous manuring, but that, for example, the *Verticillium* Wilt of Tomato is more destructive to hard, underfed plants. Nitrogenous manuring may indeed enable the plant to grow away from or to recover more rapidly from the damage caused by insect attack. The Shot-hole Borer, *Xyleborus fornicatus* Eichh., tunnels in the stem and branches of tea bushes, weakening the branches so that they are easily broken by wind or by coolies when pruning. Jepson and Gadd (15) showed that secondary mechanical damage of this kind was reduced on plots receiving nitrogenous manuring because of the more rapid healing-over of the wounds. On these plots healing-over was completed in 2·9 months as compared with 3·75 months on the control plots.

Opinions differ as to whether the effect of the separate fertilizer constituents is individual or whether it depends on the general composition of the total nutrient available to the plant. Spinks (4) concluded that though the application of mineral manures decreased susceptibility it could not counteract the application of large quantities of nitrogenous manures. A more general view favours the idea of a " balance " in the manuring, and that the ill effects of nitrogenous manuring results from dressings in which nitrogen is in excess. Thus, Schaffnit and Volk (16) found that excessive application of phosphates and potash failed to increase the resistance of the plants tested in the presence of a correspondingly increased supply of nitrogen.

The influence of the lime status of the soil upon the degree of attack by parasites is shown by the froghopper *Tomaspis saccharina* Dist., which causes Blight of Sugar-cane. Turner (17) found that, in blighted areas, the ratio of exchangeable calcium to the clay and fine silt fraction averaged 0·28–0·63, whereas in blighted areas it was between 0·11 and 0·25. The precise reason why greater damage

should be caused in the more acid soils is not clear, and, in a later paper by Pickles (18), the influence of soil factors apart from lime status is discussed.

The influence of the remaining elements known to be concerned in plant nutrition on the relations of plant and parasite is not clearly marked. Spinks (4) observed in the Woburn pot-culture experiments that wheat plants receiving small amounts of lithium salts were remarkably free from the attack of Yellow Rust and Mildew, whereas the application of small amounts of lead or zinc nitrates rendered the plants extremely susceptible. The possibility of supplying, to the plant, elements or compounds not directly affecting nutrition, but which inhibit fungus or insect attack is referred to under Plant Injection (p. 236) and the specific case of selenium (p. 221). One rather special phenomenon may be mentioned to show the possibility of the influence of trace elements in the relationship of host and parasite. Brenchley and Thornton (19) found that, for the symbiotic development of the nodule bacteria of certain Leguminosæ, the presence of boron is necessary.

The action and use of fertilizers as pest-control measures are modified not only by those factors which affect directly and indirectly the nutrition of the plant but also by those other factors which influence the parasite. So far, in discussing the action of fertilizers in their relationship to parasitic attack, only their effect on the plant has been dealt with. The companion question of the effect of manuring on those parasites which live within the soil, must be left until the question of Soil Treatment—the destruction of the pest in the soil—be considered.

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The Influence of General Soil Conditions.

Soil conditions are able to influence the extent of parasitic attack not only by their indirect effect on the action of fertilizers but by their direct effect on the growth both of the plant and parasite. The factors involved are interrelated in complex fashion and, although for convenience an attempt is made below to deal separately with soil type, soil moisture and soil temperature, the interrelationships between these various soil conditions must not be forgotten.

Soil Type.—Müller and Molz (20) concluded, from a survey of the injury caused by Yellow Rust (*Puccinia glumarum*) in Germany, that less damage is caused on heavy, deep and moist soils than on shallow dry soils ; that, whereas this rust is rarely found on marshy soils rich in mineral matter, it is abundant on soils poor in nutrients (they quoted in particular the upper Trias and shelly limestones). Howard (21), however, believed that the resistance of the plant towards rust may be affected profoundly by soil aeration. He showed that in India several of the most rust-resistant wheats are shallow-rooted, whereas most of the wheats liable to rust are deep-rooted, and cited the observation of Clouston that the Red Rot of Sugar-cane (*Colletotrichum falcatum* Went.) is common on the stiff black soils of India but is rare on the porous " bhata " soils. The reverse effect of soil aeration is noted by Butler (22) from Reunion, where the arabica variety of coffee grows well on the drier side of the island where the soil is deep, but in shallow soils it is severely attacked by leaf disease.

The type of soil frequently exerts a profound influence upon crop infestation by soil-inhabiting insects. Williams (23) stated that the Pea Thrips, *Kakothrips robustus* Uzel., is more serious on light soils than on heavy soils. MacGill (24), who reviewed the evidence upon the relationship between thrips infestation and soil type, also found that *Thrips tabaci* Lind. was less prevalent upon untilled clay soils than upon light tilled soils and suggested that the thrips were unable to emerge as easily from soils forming a hard surface as from loose soils or from clays which readily form shrinkage cracks on drying.

The general experience of French viticulturists that grape vines

growing on loose textured soils suffer less from the attacks of *Phylloxera vastatrix* than vines on heavy soils, was critically examined by Nougaret and Lapham (25) in California. They confirmed this conclusion and suggested that heavy soils, on drying, form cracks in which the root forms of Phylloxera shelter, whereas on loose friable soils, the insects are forced to come to the surface where they are unable to survive the arid conditions.

In such cases, an obvious method of avoiding damage by disease or pest is to select soil types unfavourable to the parasite. For this purpose the data now being collected by systematic soil surveying should be of great use.

Soil Moisture. For the well-being of the crop an optimum range of moisture content of the soil is necessary. If the moisture content is too low, drought may profoundly affect the susceptibility of the crop, or it may have a direct effect upon the activities of the parasite. The effect of soil moisture on the parasitism of cabbage by Cabbage Yellows (*Fusarium conglutinans*) was studied by Tisdale (26), who found that strains of host plant normally resistant became attacked if deprived of water. On the other hand, Glynne (27) showed that, in dry soil, infection of potato by *Synchytrium endobioticum* did not occur. It has been suggested (28) that a high moisture content of the soil is necessary to secure infection of the potato by this fungus as the zoospores require a film of water for migration.

The case of abnormally high soil moisture is most complex and its effects on parasitism are difficult to analyse. Thus, as badly drained soils are cold and poorly aerated, the factors of soil temperature and oxygen supply come into play, a complexity well illustrated by the work of McKinney and Davis (29) on the infection of wheat by Take-all (*Ophiobolus graminis* Sacc.). The reduction of liability to attack in soils of high moisture content is exemplified by the observation of Jones (30) that the germination of the spores of Loose Smut of Oats (*Ustilago avenæ* (Pers.) Jens.) is inhibited when the soil is saturated or, in other words, when the supply of available oxygen is reduced to a minimum.

Where the soil moisture is so small in amount that irrigation is necessary, this may be employed as a pest-control measure. Parker (31) found that the soil moisture was so important in the life of the Sugar-beet Root Aphis (*Pemphigus betæ* Doane) that an early irrigation at the first sign of wilting of the plants reduces the infestation of the sugar-beet.

The flooding of soil to asphyxiate the insects living in it was applied practically in French vineyards against Phylloxera. The method met with a certain success and its use extended for a while despite its ill after-effects on the soil.

The part played by soil selection and cultivation has been stressed most forcibly by Howard (32), who has maintained that by proper cultivation of suitable varieties the problems of Plant Protection are completely solved. Howard's faith in this hypothesis rests on his claim of its successful application in India, where, by the selection of varieties suited to local conditions and by attention to soil condition, in particular, aeration, drainage and humus content, the economic consequences of pests and diseases are said to be rendered negligible. Indeed he insists that insects and fungi serve as indicators of imperfect cultivation and therefore that their destruction by other methods, such as the use of insecticides and fungicides, is fundamentally unsound.

The possibilities of resistant strains, of the enhancement of resistance and diminution of liability to attack, have been outlined above, and despite certain difficulties, it is reasonable to prophesy that, by the development of these means, the need for reliance on other methods of plant protection will decrease. It would be as dangerous to ignore these possibilities as to condemn, in the present state of knowledge, alternative methods. There is no evidence that the applied biologist has overlooked or neglected the methods advocated by Howard and there is no justification for the adoption of his extreme view, put forward so dogmatically that more moderate observers might reasonably question whether it is based on unbiased evidence.

Soil Temperature. The effect of soil temperature and moisture upon infection by soil-borne organisms has been extensively studied, in particular, by Jones, Walker and their colleagues at the Wisconsin Agricultural Experiment Station (33). Of the fungi which require relatively high soil temperatures in order to establish infection, the Fusaria are prominent, and Jones, Walker and Monteith (34) showed that at soil temperatures below 17° C., Wilt of Cabbage (*Fusarium conglutinans*) failed to develop. Scab of Potatoes, caused by *Actinomyces scabies*, is likewise more prevalent under warm soil conditions, the optimum temperature being 20–23° C. (35).

The prevalence of Onion Smut (*Urocystis cepulæ* Frost) in the northern states of the United States and its absence from the southern states was explained by Walker and Jones (36) on the

basis of temperature relations. Onion seedlings become resistant to this disease at a certain stage of growth and, as increase of temperature promotes rapid growth, the susceptible period is passed more quickly at the higher temperatures. The fungus is also favoured by high temperatures, but Walker and Wellman (37) have shown that, above 25° C., the fungus is retarded whilst the host is stimulated, whereby the degree of attack is reduced.

The influence of soil temperature on insect pests may be illustrated from the work of Cook (38), who studied the effect of climatic factors on the relative abundance of cutworms in the soil. The optimum soil moisture content for the development of *Lycophotia margaritosa* Haw., he found to be about 60 per cent. of the total water capacity. As a heavy rainfall at a high temperature will result in the same degree of soil moisture as a lighter rainfall at a lower temperature, this optimum condition may be expressed as an equation involving rainfall and temperature. If these conditions approach this optimum over a series of years, there is likelihood of an increase of cutworm during the following year.

The direct application of this principle to plant protection would appear to be limited to circumstances when a control of soil temperature is possible, as in the glasshouse given suitable methods of soil heating. The indirect application is, however, of obvious importance and, with increasing knowledge of the effect of environmental conditions upon crop growth and the activity of parasites, successful examples of the application of the principle will become more numerous.

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CLIMATIC FACTORS

Climate, which may be regarded as the summation of weather, is of so complex a character that the study of its influence upon the prevalence of disease and pests has had to proceed upon analytical lines, each meteorological factor such as temperature, rainfall, intensity of sunlight, wind, being studied in relationship to the growth both of plant and parasite. As this work has already been reviewed by Uvarov (39) in the case of insect pests and by Foister (40) for plant diseases, it is possible to consider at once the collective influence of climate and weather on the incidence of parasitism.

Reference may, however, be made to Stoughton's analytical study of the influence of environmental conditions on the Angular Leaf-spot Disease (Black-arm disease) of cotton caused by *Bacterium malvacearum* E. M. Sm. (41). He found that the importance of air temperature for leaf infection rested in its effect on the balance between the resistance of the host, conditioned by rate of growth and maturation, and the activity of the parasite ; the main factor is therefore the average temperature throughout the incubation period. The importance of air humidity, on the other hand, was physical in character, affecting merely the time, after inoculation, during which the infection drop persists.

The importance of the collective factors which constitute climate is well shown by examples of their effects upon the distribution of pests and diseases. The distribution of the pest is governed primarily by the distribution of the host plant, but it may be found that in a particular region the climatic conditions, though still favourable to the host plant, are unfavourable to the parasite. For this reason there are areas in which control measures against a particular plant enemy are not needed.

The influence of temperature and relative humidity upon the distribution of the fungus is illustrated by the work of Peltier and Frederick (42) on the prevalence of Citrus Scab (*Sphaceloma fawcetti* Jenkins) and of Citrus Canker (*Pseudomonas citri* Hasse). They found that the growth of the scab organism was inhibited and the

injury it causes not serious, wherever a mean monthly temperature of above 75° F. prevailed, as in the Philippine Islands. Neither is the pest of economic importance in citrus-growing districts where the rainfall is below 50 inches, spread evenly over the year ; nor where there is a dry season coincident with high temperature. With regard to the canker organism they were able to conclude that the pest occurs in regions where the temperature and rainfall curves are simultaneously ascending, as in the Gulf States of America, China and South Africa ; if the rainfall curve is descending as the temperature curve ascends, as in California, the Citrus Canker is absent.

The correlation of climatic conditions and the distribution of an insect pest may be illustrated from the work of Verguin (43), who pointed out that the regions in which the Mediterranean Fruit Fly, *Ceratitis capitata*, is a serious pest are within the January isotherm of 10° C. on the world map. The insect appears to be incapable of establishment in areas where a suitable supply of host plants is not available throughout the year or where the mean monthly temperature falls to, or below, 50° F. for three consecutive months of the year (Back and Pemberton, 44).

The correct bio-climatic mapping of the distribution of a particular host-parasite complex forms a rational basis for the application of restrictive control measures. Between regions of dissimilar climatic features in so far as they affect a particular disease or pest, it is unnecessary to impose restrictions upon the interchange of host material. Between regions of similar ecological and climatic features there is, on the other hand, every reason to adopt restrictions such as the prohibition of imports or the inspection, quarantine or fumigation of imported plant products.

The phenomenon that the climatic conditions may be unfavourable to the parasite, while still favourable to the host plant, is observed more easily as a result of the climatic changes due to altitude. An excellent example is offered by Dowson (45) on the cultivation of coffee in Kenya. At altitudes of 6,000–7,000 ft., the climate is still favourable for coffee-growing but unfavourable to the organism (*Hemileia vastatrix* Berk. & Br.) causing Coffee Rust, and the disease has no serious consequences. At 5,000–6,000 ft. the disease is easily controlled by the application at the right time of any dilute fungicide ; at 4,000–5,000 ft. regular spraying with stronger fungicides is necessary to secure control of the disease. Below 4,000 ft. the conditions are so favourable to the rust organism

that, even where the rainfall is suitable, coffee-growing becomes unprofitable.

A prerequisite to the deduction of correlations between pest and disease distribution and climatic conditions is a suitable method of expressing graphically or statistically the two variables concerned. The representation of climatic factors by a graph on which the mean temperature and mean relative humidity for each month are plotted on the two ordinates and the points are joined in the sequence of the months was adopted by Shelford (46) for entomological purposes. For phytopathological purposes, Tehon (47) employed a three-dimensional graph in which temperature and precipitation were plotted along the horizontal ordinates and the severity of attack was plotted vertically. By such a method, Tehon was able to trace interesting relationships as, for example, in Curly Top of Sugar-beet, a virus disease transmitted by the Beet Leaf-hopper, *Eutettix tenellus* Baker. The abundance of the insect is conditioned by relatively high temperatures and high rainfall, whereas the appearance of the disease is dependent on low rainfall. The range of the leaf-hopper is therefore more extensive than that of the disease it transmits.

There is a danger that the simplification effected by graphical and statistical methods may lead to erroneous generalizations, as the climatic data used are but averages for a wide range of time and locality. An instructive example of the effect of local variations not expressed in the data is quoted by Uvarov. Graf (48), in attempting to correlate the distribution of the Mexican Bean Beetle, *Epilachna varivestis* Muls., used data supplied by the meteorological stations of Mexico and the neighbouring states of the United States. He concluded that climatic factors did not determine the distribution of the beetle. Sweetman (49) pointed out that, in arid regions, the beetle was confined to irrigated areas, the humidity of which differed from the average for the area.

Further, the numbers of short-lived organisms such as fungi and insects may undergo violent fluctuations dependent upon annual variations of climate. It is well known that there are years in which the injury caused by a particular disease or pest is of extreme severity whereas, in other years, control measures are scarcely necessary.

Much can be learnt of the reasons for these fluctuations by the study of past epidemics in relation to climatic conditions. Lambert (50), in such a study of the history of Stem Rust of Wheat (*Puccinia*

graminis tritici (Pers.) Erikss. & Henn.) in the Mississippi valley, was unable to obtain evidence of meteorological conditions specifically associated with severe outbreaks. Peltier (51) was more successful in a similar study in Nebraska. The factors he found necessary for an epidemic of Stem Rust were : (1) suitable conditions for wind transmission of the uredo stage of the fungus from Texas and for the establishment of infection in Nebraska, (2) winter wheat in Nebraska at the " heading " stage of growth during or after the first week of June and (3) an extended fruiting period for the fungus, namely, optimum temperatures and an evenly distributed rainfall above the normal. Epidemiology of this type will supply information which must ultimately be of the greatest value in plant protection.

At present the practical application of epidemiology is confined mainly to the forecasting of pest or disease outbreaks, whilst knowledge of the relationships between climatic conditions and the degree of attack is applied to the protection of crops growing in the glasshouse, where a control of climatic factors is possible.

The Meteorological Forecasting of Epidemics. Reliable forecasting of the likelihood of outbreaks of disease or of abnormally heavy insect infestation is of obvious value to the grower, especially if such forewarnings enable him to be better prepared with means of combating the disease or pest. In the use of insecticides and fungicides, for example, correct timing of the application is frequently a factor of efficiency. This timing is generally effected by employing some conspicuous event in the life-history of the crop plant, e.g. petal-fall, as a criterion. There are cases, as in the application of protective fungicides against Blight (*Phytophthora infestans*) of potato, when there is no suitable phenological indicator and, in all cases, additional methods of correct timing would be of great value.

Schemes for forecasting, from meteorological evidence, the incidence of disease and pests so that the grower may begin direct combative measures are in operation in several countries. In Holland (52) warning is given of the likely spread of Potato Blight, the criteria being, (1) a night temperature below dew-point for at least four hours, (2) a minimum temperature above 10° C., (3) a mean cloudiness on the following day of not less than 0·8 and (4) a rainfall during the following twenty-four hours of at least 0·1 mm. These requirements afford an adequate explanation of the common association, in this country, of Potato Blight with dull

weather in July and August, for the conidia and zoospores of the fungus only germinate under moist conditions at an optimum temperature of 70°–74° F., the conditions prevailing here during dull weather in these months.

In localities where the important primary source of infection of Apple Scab (*Venturia inæqualis*) is from perithecia, meteorological forecasts in conjunction with phytopathological evidence are utilized to determine the most suitable date of spraying (53). As the discharge of ascospores from the ripe perithecia only occurs after a period during which the leaves are thoroughly wet, the meteorological factor is the rainfall during the spring months. In this country, the perithecia have not been shown to be the primary source of infection (54, 55) nor are the weather conditions during the spring months of so continuous a character that it is possible to time spray application on the basis of meteorological forecasts.

The Control of Temperature and Humidity Relationships. In the glasshouse it is often possible to modify temperature and humidity in a manner such that the activities of the parasite are checked without severe interference with the well-being of the plant. Bewley (56) took advantage, in this manner, of the importance of the air and soil conditions in combating the Verticillium Disease of Tomatoes. The wilting of foliage, symptomatic of this disease, is due to toxins produced by the fungus and translocated in the water supply of the plant. As soon as it is proved that *V. albo-atrum* R. & Br. is the pathogen, precautions are taken to reduce to a minimum water movement in the infected plants by shading, by increasing the humidity of the atmosphere by overhead damping yet maintaining the soil dry, by raising the temperature of the house above 25° C. (77° F.). These conditions held for a fortnight or so will permit the wilted plant to recover and produce a normal crop.

The damping off of tomatoes (*Phytophthora* spp.) is aggravated by high water content in air and soil. A regulated watering of the seed boxes to keep the soil uniformly moist, combined with efficient ventilation permitting the rapid drying of the surface soil, will help to keep this disease under control. The control of Tomato Leaf-Mould *Cladosporium fulvum* Cke., by cultural operations is discussed by Small (57). As 22° C. is the optimum temperature for this fungus and higher temperatures are unfavourable to the tomato, the temperature should be kept below 22° C. during March and April. Further, as the disease is favoured by high humidity, the relative humidity of the glasshouse should be kept below 75 per

¢ent. on warm nights and the ventilators should be opened during
dull or rainy weather. The plants should be watered early in the
day and preferably only on fine days. Finally, air circulation should
be promoted by open ventilation and by pruning the lower foliage
of the plants.

By cultural operations it is frequently possible to modify tem-
perature and humidity relationships of crops growing in the open.
The relative humidity may be reduced, for example, by more open
planting, by clean cultivation or by pruning. In the apple orchard,
the removal of low branches and of rank undergrowth provides
" bottom " ventilation and tends to reduce the severity of scab
attacks. The stripping of the lower leaves from the bines is a
common practice in hop gardens, and designed to remove a habitat
favourable to the development of aphis. Kirkpatrick, who quoted
(58) the example of the pruning of coffee in order to promote air
circulation and thereby to secure a lowering of the relative humidity
within the crop as a defence against Coffee Mealy Bug, *Pseudococcus
citri* Risso., has investigated (59) the effect of various cultural
practices upon the local climatic conditions within the coffee
plantation.

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The Modification of Time of Sowing.

Not infrequently the attack of the parasite occurs only during a period of short duration in the life of the crop plant. It may therefore be possible, by cultural methods, to ensure that, during this period, the plant is at a stage when infection or attack will cause least damage. The principle of such methods thus becomes the regulation of crop growth so that the period of greatest susceptibility is not coincident with the period of greatest liability.

The proper preparation of the seed bed to enable prompt germination and rapid growth of the seedling, a suitable manuring, but more important, a regulation of the date of sowing, are the main methods employed. The reduction of the amount of damage caused by the Gout Fly of barley (*Chlorops tœniopus*) by the use of phosphatic fertilizers which hasten maturity has already been mentioned. Frew (60) also suggested the early planting of spring barley for the same reason. A parallel example is provided by the work of Cunliffe and his colleagues (61) on the biology and cultural control of Frit Fly (*Oscinella frit* L.). This pest of oats, under English conditions, has three generations each year. Flies of the first generation oviposit on oat seedlings and attain maximum numbers towards the end of May. Ovipositing flies of the second generation are most abundant at the middle of July. The oat plant is most susceptible at the two- and three-leaf seedling stage and at the time of fertilization and becomes resistant after it has reached the four-leaf stage and after the grain has grown to half its normal size. It follows therefore that winter-sown or early spring-sown oats stand a better chance of resisting attack than oats sown late in March or in April. The early-sown oats reach the four-leaf stage prior to the period of maximum oviposition by the first-generation flies and escape the attack of the second swarm of flies until the grain has reached its resistant stage.

When the plant is most susceptible in its seedling stage, the effects of too advanced a date of spring sowing may be nullified by the slower growth made by the plant in early spring. Severin (62), in the case of the Curly Top of Sugar-beet, a virus disease which appears to be transmitted from diseased to healthy plants by the Leaf-hopper *Eutettix tenellus*, stated that in California, in localities outside the fog belt, the early planting of the sugar-beet was the only method of preventing severe losses. If the plant be large by the time the insect invades the field, a commercial crop can still be produced.

In a similar manner a delayed autumn sowing may enable the plant to escape infection. Thus McKinney (63) shows that early-sown winter wheat is more severely affected by the Helmintho-sporium disease than is late-sown winter wheat—an observation in agreement with trials in soil-temperature tanks, which have shown that high soil temperatures favour the disease. Howard (64) gives an analogous example in the destruction of wheat by termites at Bikar (India). If the wheat is sown a few days too early the seedlings are rapidly destroyed by termites, a fact attributed to the high soil temperature, for if planted twelve days later, the furrows being left open meanwhile to aid the cooling of the soil by evapora-tion, the damage becomes negligible. Perhaps the most discussed example of this means of control is afforded by the relation between the date of sowing of winter wheat and the prevalence of Bunt caused by two closely related species, *Tilletia caries* (DC.) Tul. and *T. fœtens* (Berk. & Curt.) Trel. It has generally been found that if sown either very early or very late, the crop is freer from the disease than the crop sown in the intermediate period. The litera-ture and general aspects of this example are discussed by Reed (65).

The avoidance of insect attack by late autumn sowing is illustrated by American experience of the control of Hessian Fly (*Mayetiola destructor*). One method is to sow wheat so late that the susceptible seedlings do not appear above ground until the autumn generation of the fly has died down. The date of sowing must be sufficiently advanced for the wheat to have made enough growth to enable it to survive winter. Hence, in certain States, the authorities suggest "fly-free" dates which, though the dates of maximum emergence of the flies, are those after which sowing will give the minimum infestation. In Illinois (66), the fly-free dates in the northern parts are 18 September and, in the south, 9 October. The fixing of the fly-free date for a given locality to one definite day may, in abnormal seasons, prove ineffective. Drake and Decker (67) recorded that in 1930 the emergence of the autumn brood was not completed until after the normal date and that the progeny of the late emergents survived winter. Drake and his co-workers (68) had previously suggested that the fly-free date should be determined by actual observation of the day of maximum emergence from puparia collected in the field.

In other cases, late spring sowing may be a means of avoiding attack. It has frequently been observed, in England, that carrots sown early—e.g. in March—are more severely infested with Carrot

Fly larvæ (*Psila rosæ* F.) than those sown later—e.g. in May. Fryer (69) attributed this to the fact that the first brood of the Carrot Fly has partially died off by the time the May-sown carrots are above ground—the stage of growth when the fly makes its attack.

The maturation of the crop before the attack of the pest may further be accomplished by the use of early maturing varieties. Dowson (70) has shown that at Nairobi, where there are two rainy seasons in the year, it is possible to grow early-maturing varieties of wheat in both.   By this means it is also possible to escape Black Rust (*Puccinia graminis*), which usually appears late in the season. The Australian wheat " Florence," which matures in Nairobi in four months after sowing, when sown early enough escapes injury, whereas another Australian wheat " Bobs," maturing in six months after sowing, is always attacked by the rust. If the Florence variety be planted two months later, so as to mature at the same time as the Bobs variety, it is equally infected.

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CHAPTER IV

BIOLOGICAL CONTROL

In the previous chapter, the utilization of the influence of external factors of a non-biological character on the host-parasite relationship of crop-plants has been discussed as a principle of plant protection. The present subject, biological control, is the use of biological factors to this end. The object of biological control is, therefore, to augment the deleterious effect of biotic factors upon the development of the parasite. This effect may be increased by the reduction of the influence of factors which prejudice the biotic factors or, more importantly, by the introduction of additional biotic factors. Biological control may thus be interpreted as the encouragement of beneficial organisms already existing in a locality and the introduction to that locality of new species of beneficial organisms.

The encouragement of beneficial organisms already established in a locality is, in general, limited to their protection from unfavourable conditions and from their parasites, called at this stage hyperparasites. The development of insectivorous birds, for example, may be assisted by the provision of water or of nesting-places and by protection from hawks, cats, egg-stealers—" hyperparasites " as it were. The measures which may be taken are limited by their expense and compared with the astonishing results sometimes secured in the second group of biological-control methods—the introduction of new species—the success of such measures is small.

Those biological-control methods which involve the purposeful introduction of new species of organisms are subject to certain general features which may well be discussed at this point. The introduction of new plant species, an everyday occurrence in the domains of agriculture, horticulture and floriculture, offers no practical difficulties if the conditions of climate, nutrition, etc., are suitable for the healthy development of the plant. Indeed, in some cases, in which it has later been found that the pests of the exotic

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plant are absent from its new habitat, conditions have been so favourable that the introduced plant has exceeded the limits of its usefulness and has actually become a pest to other crops. Some examples of this occurrence are discussed under the biological control of weeds. In other cases, pests of the exotic plant have been introduced which, because of the absence of their usual hyper-parasites, have likewise developed to such an extent that they have threatened the cultivation in their new sphere of action, not only of their original host but even of fresh hosts. By the introduction of the enemies of the pest from its old habitat a successful control in such cases has often been established.

It will be seen at once that such cases involve the absence of organic factors which contribute towards the establishment of the native natural balance. With modern means of transport the chances that these factors will be accidentally introduced into the new locality increase rapidly with time and it may well be assumed that in due course the missing factor will find its way into the region where its host has thrived. Even so it is quite possible that, although present, its effect will be negligible compared with that in its original home, because of the unfavourableness of its new environment.

The chance of the absence of a particular organic factor, i.e., the scope for the use of this form of biological control, will therefore depend upon the time that has elapsed since the introduction of the host and/or its pests. Thus it is that the outstanding successes of the method have occurred in localities where the disturbance of the original ecological conditions has been comparatively recent—e.g., in the New World and in Australasia.

Again, the chance of absence of these factors will be dependent upon the relative isolation of the locality from those in which they are present. Such isolation is to be found, for example, in the Hawaiian Islands or New Zealand, where the surrounding sea provides the isolating barrier, or in California, or Western Australia, where the barrier on one side is the ocean, on the other, desert or mountain. " Ecological islands " of this type may also be on the smaller scale noted by Myers (1). In the West Indies and on the neighbouring mainland of South America, Myers found clearly defined ecological islands, bounded by forests, rivers or swamps, within which large areas of cultivated crops are of recent introduc-tion. It is evident that, in such a circumscribed area, even an indigenous insect may become a pest of the cultivated crop under

conditions where beneficial organisms, though present in the area, are helpless.

It is in ecological islands of these two types that the possibilities of biological control are greatest and where the widest scope has been found for the introduction and encouragement of beneficial organisms.

The principles of biological control have been discussed by Thompson (2) and by Sweetman (3) but, to avoid further abstractions, concrete examples of the methods will be given, special points and difficulties being discussed as they appear.

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HIGHER ANIMALS

With the higher animals, the scope of biological control is limited entirely to the encouragement of those which are beneficial because of their influence upon injurious organisms. For, with their migratory powers and their tolerance towards external conditions, the introduction of higher animals into new territory would follow, almost automatically, the penetration of civilization.

The value of certain birds as the natural enemies of voles and mice has been recognized from early times. These rodents, of which the Short-tailed Field " Mouse " (the animal is really a vole), *Microtus agrestis*, is perhaps the most notorious, at times increase to such an extent that they cause great damage. For example, in 1892 in Scotland the plague was sufficiently serious to warrant a Government investigation (4). The causes contributing to the occurrence of such plagues are considered below. Under normal conditions, however, the Kestrels and Short-eared Owls play a great part in the checking of the increase of these pests.

The insectivorous birds are undoubtedly of considerable importance in the establishment of the natural balance of insects. For instance, it has been found in the United States that thirty-six kinds of birds feed upon the Codling Moth. McAtee (5) calculated that, in some localities, from 66 to 85 per cent. of the hibernating larvæ are destroyed by this means. In Holland (6) the value of birds as pest-controllers is reflected in the establishment of a special section of Ornithology in the organization of the Phytopathological

Service. Van Poeteren remarked that the " protection of insect-eating birds is the most important form of biological attack we apply in our country."

That special encouragement of any particular species of bird should only follow from an accurate knowledge of its life activities is shown by the case of the Buff-backed Egret (*Ardea ibis* L.) recorded by Kirkpatrick (7). This bird, once abundant in Egypt, was killed off so thoroughly by plume-hunters that, by 1912, only two small colonies of a few pairs remained. It was at that time thought that the bird played an important rôle in the control of Cotton Worm (*Prodenia litura* F.), for popular opinion claimed that, prior to the recognition of the value of its feathers, these birds formed a prominent feature of the landscape, picking up larvæ and pupæ from the newly turned soil (8). A law was then passed for the protection of the more important insectivorous birds by the provision of sanctuaries and by the infliction of penalties upon the bird-hunters. The egret, by 1924, had increased in such abundance that it threatened to become itself a pest. Stomach examination revealed that the claim of the value of the bird as a biological-control factor was, if not erroneous, most exaggerated.

The advocates of Bird Protection claim that graminivorous birds are beneficial in that they consume weed seeds. It would appear, however, that the substantiation of this claim is difficult, for mere stomach examination is an untrustworthy criterion. The hard seed-coats of the more pernicious of our weeds may prevent their digestion and the seed will pass through the intestine.

Mention must also be made of a system introduced by W. Rodier, in New South Wales, for the suppression of rabbits which had become so numerous that the labour required to render control by trapping successful was not available. Rodier tested the idea of killing, of the trapped animals, only the females. The males were released in the hope that the remaining females would be pestered out of successful breeding by the superabundance of males.

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INSECTS

Insects versus Insects. The first suggestion that entomo-phagous insects could be used for the purposes of plant protection appears to have been due to Noteriani (9), whilst the first recorded adaptation of the method, according to Trotter (10), was the employ-ment of the Carabid Beetle *Calosoma sycophanta* L., by Boisgiraud in 1840, (against Gypsy Moth (*Lymantria dispar* L.) on poplars growing around Poitiers. The early history of the subject has been reviewed by Howard and Fiske (11).

The classical example of the use of a beneficial insect is the control of a scale insect, the Cottony Cushion or Fluted Scale, *Icerya pur-chasi* Maskell, by the Lady-bird Beetle *Novius* (*Vedalia*) *cardinalis* Muls. Marlatt (12) recorded how this scale insect was introduced into California from Australia, in 1868, on imported plants of *Acacia latifolia* Desf. The insect, finding in the orange groves of California an eminently suitable habitat, increased with such rapidity that by 1886 it threatened the entire citrus industry of the Pacific coast. The insectidal sprays then available proved no check. In 1889 Koebele was sent at the suggestion of the Division of Entomology to Australia to investigate the reason for the relative unimportance of the insect there. He returned with its natural enemy the Lady-bird Beetle *N. cardinalis*. In a very short time this beetle had practically exterminated the Fluted Scale. So good a control was obtained that in 1900 Marlatt wrote, " The remedy for this scale is always and emphatically to secure at once its natural and efficient enemy the *N. cardinalis*."

It is of interest to see how true Marlatt's statement has proved. The Fluted Scale has since appeared in the majority of citrus-growing localities. Mendes (13) reported the occurrence of Fluted Scale on acacias in Portugal in 1910. The appearance of *N. cardi-nalis* followed and within a year the Fluted Scale was destroyed by the predator. Berlese (14) in 1916 was able to state that at that time the Fluted Scale, which prior to the discovery of *N. cardinalis* was a great menace to citrus crops, had no longer any agricultural importance whatever. The high efficiency of *N. cardinalis* is prob-ably ascribable to its great activity both as a larva and adult, its freedom from hyperparasites and its high rate of reproduction in comparison with that of the scale insect.

A less direct but equally effective example of the use of beneficial insects was recorded by Taylor (15). In Fiji a Hispid beetle,

Promecothea reichi Baby, rarely became a serious pest of the coco-
nut palm as it was held in check by several native natural enemies.
This check was effective because the generations of the beetle then
overlapped so that the various developmental stages occurred
together and the several enemies were able to maintain a condition
of " multi-stage " parasitism.   In 1921 the mite *Pediculoides ventri-
cosus* Newp. was recorded in certain parts of Fiji attacking the
larvæ, pupæ and adults of the beetle so successfully that the number
of the latter was reduced practically to zero.   The mite population
likewise declined and, as a result, the beetle population again rose,
but this time with no overlapping stages, a one-stage condition in
which the indigenous parasites were no longer able to maintain a
biological control.   To restore this control it was necessary to
introduce a parasite effective in the presence of the mite and it was
deduced that the successful parasite should have the following
characteristics : it should tolerate the climate of Fiji ; it should be
an internal parasite of the larval and pupal stages ; it should
have a biotic potential (i.e. egg-capacity × sex-ratio) of at least
twenty and complete a generation in not more than one month,
thus ensuring a favourable ratio between numbers of parasite
and pest ; finally, when adult, it should live for at least three
weeks.   A survey of the parasites of an allied Hispid beetle in
Java led to the selection of *Pleurotropis parvulus* Ferriere, not
the most effective in Java of the parasites found there, but of
greater promise under Fijian conditions.   Within a year of the
introduction of *P. parvulus* into Fiji, *P. reichei* was no longer
a pest.

The value of this method of pest control, which is most striking
in the successful introduction of absent beneficial insects, requires
no stressing.   Once established, the activities of the beneficial
insect will reduce or even eliminate the need for the more expensive
artificial-control measures such as spraying.   Furthermore, this
expense is an annual item, but the expense of the importation of
beneficial insects ceases with establishment.

The difficulties which may attend the establishment of a beneficial
insect are illustrated by the attempts to utilize, in this country,
Aphelinus mali Hald. for the control of Woolly Aphis (16).   The
introduction was begun in 1928 and continued, at a number of
centres, until 1931, by which time it appeared to have become
established at one centre.   The unfavourable weather conditions
of 1931 made it doubtful, however, whether a permanent establish-

ment of *A. mali* was possible or whether reintroduction from artificially protected colonies would be necessary.

The artificial carrying over of the beneficial insect has sometimes been found profitable as is recorded by Smith (17). The Black Scale (*Saissetia oleæ* Bernard) is controlled in South Africa by parasites, amongst which *Aphycus lounsburyi* How. plays a prominent rôle. In California, however, the adult Black Scale becomes scarce in July and the young insects surviving are too small to serve as hosts for this parasite until after the second moult, which does not occur till February. The parasite is therefore without a sufficient food supply for six months and can be maintained only by an annual liberation.

Similarly, for the control of various of the citrus mealy bugs (*Pseudococcus* spp.) of California, the Lady-bird Beetle (*Cryptolœmus montrouzieri* Muls.) has been introduced. Armitage (18) has shown that the permanent establishment of the beneficial insect is prevented by adverse weather conditions. The winters are too cold for the mealy bug to breed yet not cold enough to force the lady-bird to hibernate. As in the former example, the parasite is without an available host during this period and it is necessary artificially to ensure its overwintering.

The principle that the greatest opportunities for the utilization of biological control are to be found under conditions of recent ecological disturbance is applicable to glasshouse crops and an example, in this country, is afforded by the control of Greenhouse Whitefly *Trialeurodes vaporariorum* West. In 1915 (19), a Chalcid (probably *Encarsia partenopea* Masi., 20) was discovered by Fox Wilson and bred for the control of Whitefly but, by mischance, was eventually lost. In 1926 a related Chalcid, *E. formosa* Gagan, was found by Speyer (20) and successfully reared for distribution to growers. It is necessary to maintain the Chalcid through the winter, but so successful a control of Whitefly is achieved (21) that its utilization as a control measure has now become routine.

The encouragement of a beneficial insect by means other than artificial rearing is illustrated by the example of the mealy bug *Pseudococcus lilacinus* Ckll., which had become a serious pest of coffee in Kenya (22). As its normal enemies were already present, it became a question why the mealy bug should be so serious a pest. The cause was ultimately found in the presence of a small Myrmecine ant (*Pheidole punctulata* Mayr.). The association of ants with scale insects and aphides has been the subject of much

speculation and it is usually assumed that the ants attend and protect these insects for the sake of the " honeydew " they secrete. In Kenya it was observed that, in the absence of the ants, the mealy bugs only occurred spasmodically and it was repeatedly proved that, if the ants were denied access to the infected coffee tree, the mealy bug was soon destroyed by its enemies.   The success of biological control, in this case, becomes dependent upon the satisfactory control, by other means, of the ants.   For this purpose, the banding of the coffee bushes with a special type of coal tar repellent (23) was recommended (24).

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Insects versus Weeds.   The first attempt to control weeds by their insect pests was made by Koebele in 1898 (25).   About fifty years previously the thorny species of Lantana (*L. camara* Cham.) had been introduced into the Hawaiian Islands from Mexico as an ornamental shrub.   The plant increased at an alarming rate and became a menace to the pastures of the low-lying regions.   Koebele, from 1898 onwards, introduced many of the insects which in its original home contributed to its suppression with such success that now, in the drier regions, further control measures are unnecessary.

In Queensland and New South Wales, the Prickly Pear (*Opuntia* sp.) introduced as a botanical curiosity, has spread with such rapidity that it is estimated that sixty million acres of grazing country have been rendered useless by the weed.   In its original

habitat in America, the Prickly Pear is held in check by many insect species and the Prickly Pear Board of Australia (26) has sought to obtain the same natural control by the importation of selected pests from America. An early experiment, the introduction of the cochineal insect *Dactylopius ceylonicus* Green, from Ceylon, was successful in controlling *O. monacantha*, but was ineffective against *O. inermis* and *O. stricta*, the two most noxious species of prickly pear found in Australia. The related species of cochineal insect, *D. opuntiæ* Call., proved more successful but is unfortunately itself attacked by the Lady-bird Beetle *Cryptolæmus montrouzieri* which was mentioned above as a beneficial insect for the control of mealy bugs. Of the other beneficial insects imported during the campaign against Prickly Pear, the moth *Cactoblastis cactorum* Berg. and, to a lesser degree, the red spider *Tetranychus opuntiæ* Banks, have proved the most effective and not only has the rate of spread of prickly pear been checked but about 25,000,000 acres of good agricultural land has been reclaimed.

It will be noted that the two examples quoted are concerned with the control of plants of somewhat unusual characters and that the beneficial insects used are specifically adapted to such cacti-like hosts and are unlikely to attack plants of economic importance. In cases where the weed is related to crop plants, there is a danger that the phytophagous insect may infest the related crop plant in its new environment. The greatest caution is therefore necessary and importation should only follow a complete experimental demonstration that the beneficial insect is unlikely to become a pest. The procedure of such trials has been discussed by Davies (27).

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Miscellaneous Beneficial Animals.

Although no successful example of the use of animal organisms lower than the insects can be recorded, there are indications that such organisms contribute to natural control. Filinger (28), for instance, observed that the centipedes *Lithobius forficatus* L. and *Poabius bilabiatus* Wood prey upon the Symphylid *Scutigerella*

immaculata Newport and, in one glasshouse, appeared to have controlled this reputed pest.

The records of nematodes parasitic upon insects have been summarized by Bodenheimer (29). Thorne (30) examined the status of the genus *Mononchus* in relation to the sugar-beet nematode, *Heterodera schachtii* Schmidt, but concluded that, because of their time of reproduction and food habits, *Mononchus* spp. were of doubtful economic importance.

A remarkable example of parasitism, recorded by Goodey (31), is afforded by the nematode *Tylenchinema oscinellœ* Goodney which infests the Frit-Fly, *Oscinella frit*, causing sterilization in both sexes by preventing the development of the reproductive organs.

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<div align="center">*FUNGI*</div>

Fungi versus Insects. The first observation on fungi parasitic upon insects appears to be due to Metchnikoff who, in 1878, investigated the fungi which attack the Lamellicorn Beetle, *Anisoplia austriaca* Hobst., which is of considerable economic importance in southern Russia. He isolated, among others, the Green Muscardine (*Entomophthora* (*Metarrhizium*) *anisopliœ* Sorokin).

Many species of entomogenous fungi have since been noted and their importance as factors in the natural control of insects has been the subject of frequent comment and controversy. It is agreed that, at times, such fungi exert a great influence. For example, Vassiliev (32) estimated that, in 1902, the above-mentioned fungus was, in certain localities, responsible for the death of 60–70 per cent. of the larvæ of *Anisoplia austriaca*. Burger and Swain (33) reported that, during a period of extreme heat in southern California, 88 per cent. of the Walnut Aphis, *Chromaphis juglandicola* Kalt., were killed by a fungus *Entomophthora chromaphidis*, though the aphis again developed rapidly after the hot spell.

Attempts to apply such fungi for the biological control of insect pests by their introduction into localities where they are absent, have never met with the success of the insect versus insect work. There are, however, a few isolated examples : for instance, Dunstan (34)

was able to show that in Europe the chief factor contributing towards the natural control of the Apple Sucker (*Psyllia mali* Schr.) was a fungus disease caused by *Entomophthora spærosperma* Fres. The sucker had caused much damage in Canada since its first appearance in 1919 and the liberation of the fungus, after artificial culture, resulted in a notable reduction of the pest, especially in the Maritime provinces where climatic conditions were highly favourable to the development of the fungus.

An extensive effort has been made by the Florida State Plant Board to secure the establishment of a number of entomogenous fungi in the citrus plantations. Speare (35) cited the fungus *Entomophthora fumosa* as the main factor in Florida in the natural control of the Citrus Mealy Bug (*Pseudococcus citri*), while Uphof (36) gave a list of the fungi which may serve to check the ravages of the various scales to which the citrus fruits are liable. Watson (37) claimed that the importance of these entomogenous fungi is demonstrated by the large increase of scale insects when the citrus trees are sprayed with Bordeaux mixture ; the fungicide by destroying the beneficial fungi assists the multiplication of the injurious insect. As confirmatory evidence he gave the average counts on ten oranges and fifty leaves from each plot :

	Scales on fruit.			Scales on leaves.		
	Sept. 1.	Oct. 25.	Nov. 28.	Sept. 1.	Oct. 25.	Nov. 28.
Check .	25·7	52	70	33·4	10	8
Sprayed	370·0	2559	6835	175·6	155	194

The rapid multiplication of the scale when unhindered by the presence of the fungi gives some indication of the importance of the fungi in the natural control of the citrus scale insects.

The practical importance of the fungi as biological-control agents would appear to be dependent to an extent far greater than observed with the use of beneficial insects, on the favourableness of the external factors and on the factors affecting the spread of the organism. Petch (38) has summarized the position thus : " If entomogenous fungi exist in a given area, practically no artificial method of increasing their efficiency is possible. If they are not present, good may result from their introduction if local conditions are favourable to their growth ; but on the other hand, their absence would appear to indicate unfavourable conditions. It would seem that a fungus makes little progress until the insects are excessively numerous . . . when, for reasons not known, an epidemic of fungus disease breaks out. . . . The problem which has yet to be solved

by those who wish to control insects by means of fungi, is how to create an epidemic at a time when such an epidemic would not occur naturally.   The evidence indicates that it is not possible to accomplish that by the mere introduction of the fungus or by spraying spores from natural or artificial cultures."

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Fungi versus Fungi.   The practical utilization of the antagonistic action of one fungus upon another was first suggested by Millard and Taylor (39), who sought to explain the control of Potato Scab (*Actinomyces scabies*) by green manuring.   This fungus is able, under certain conditions, to live saprophytically, feeding upon the dead organic matter of the soil.   Millard and Taylor considered that green manuring would therefore at first produce a rapid increase of the fungus.   Not only, however, will this optional saprophyte benefit, but also other obligate saprophytes of this species.   A competition for the available food will finally result from which it is assumed the stronger obligate saprophytes will survive and the weakly saprophytic *A. scabies* will be depressed.   They examined this hypothesis by pot-culture experiments which clearly showed the inhibitory effect on the scab organism of inoculation with obligate saprophytic *Actinomyces*, a result they found was not due to the setting up of an unfavourable soil reaction (see p. 290) but to a competitive action.

The adverse effect of the development of saprophytic fungi on that of the parasitic soil fungi may be exerted in a variety of ways, well illustrated from Garrett's (40) work on the biological control of *Ophiobolus graminis*, the cause of the " Take-all " Disease of wheat.   This fungus spreads in the soil only along the roots of its host plant, but can exist in a resting stage in the dead host tissue. Garrett obtained evidence that the rate of growth of the fungus along the roots decreases with increase in the concentration of carbon dioxide in the surrounding soil atmosphere.   This concentration is determined by microbiological activity in the immediate zone and by the rate of diffusion of the gas from that zone.   The

growth of *O. graminis* can therefore be inhibited, (1) by encouraging microbiological activity by the application of organic matter, and (2) by cultivation aimed at the close packing of the soil around the roots, e.g. a firm seed-bed. The control thus obtained is growth-inhibiting or fungistatic as distinct from the control obtained of the resting stage of the fungus. Garrett showed that, in the latter stage, the destruction of the fungus can be accomplished by the addition of organic matter poor in nitrogen, e.g. rye-grass meal, wheat straw. He suggested that the number of saprophytes is increased by the supply of nutrients but, lacking nitrogenous food, they assimilated the mycelium of *Ophiobolus* thereby exerting a fungicidal action. Another type of fungicidal action was envisaged by Brömmelhues (41), who attributed the inhibition of the growth of *O. graminis* in culture by fungi such as *Helminthosporium sativum* Pammel, King and Bakke and *Penicillium* sp. to the secretion, by the antagonistic fungus, of a thermostable and readily diffusible toxin.

The phenomenon of antagonistic action is of manifest importance with soil-inhabiting fungi and not only may it prove of great value as a basis for biological control but it may provide explanations for certain obscure points in the pathogenic character of soil fungi. These fungi are of great economic importance in agriculture and are not always readily controllable by cultural methods.

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BACTERIA

Bacteria versus Insects. The existence of bacterial diseases of insects also appears to have been first noted by Metchnikoff (1878), who observed that diseased larvæ of the beetle *Anisoplia austriaca* were infected with *Bacillus salutaris*. A number of bacteria to which insect diseases can be traced have since been isolated and described, but attempts to utilize these bacteria as a means of insect control have met with but little success. One well-tried example is the bacillus isolated in 1910 by d'Hérelle (42), who, present in Yucatan during a serious invasion of the locust

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Schistocerca pallens Thumb., observed that a large number died from a diarrhœa. From the intestines of the diseased insect he isolated the *Coccobacillus acridiorum* d'Hérelle and suggested the possible use of the organism for the control of locusts in other countries. Although there were cases in which his method gave satisfactory results, the majority of workers were unable to substantiate the original claims. Béguet (43) in a report on trials with *C. acridiorum* extending over a number of years against the locust *Schistocerca gregaria* Forsk., most common in Algeria, stated that, although the distribution of virulent cultures of the bacillus, sprayed on the food of the locust, had always started an epidemic, this epidemic had never brought about a complete control of the locust. It is of interest to note that to account for this incompleteness of control, Béguet (44) suspected the existence of a natural infection which produced immunity. McKillop and Gough (45) tested the *C. acridiorum* as a control agent in Egypt but found it unsuitable. In South Africa Lounsbury (46) tested the use of *C. acridiorum* against the non-migratory grasshopper *Zonocerus elegans* Thumb. He concluded that the method can only be used as a supplement to the older method of poison baits and pointed out the objection that, whereas the poison baits are always at hand and simple to use, the preparation of a culture of the requisite virulence is lengthy and requires a skilled operator. Finally, from South America, Kraus (47) reported a failure and even raised doubts as to the pathogenic nature of the bacillus.

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Bacteria versus Higher Animals. Against rodents, however, the use of disease-producing bacteria has met with more success. Löffler (1892) isolated from diseased field mice the *Bacillus typhi-murium* and employed this bacterium to create an artificial epizootic among field and house mice. The next year Danysz (48) discovered further pathogenic bacteria, of which at present some ten or more are known. In general, these bacteria are of the Gaertner group of *Bacillus enteritidis*, causing an inflammation of the intestines.

The usual method is to use the bacterial culture as a poison bait, and there are on the market nowadays a number of such so-called virus preparations (see 49). Splendore (50) recommended the sub-cutaneous inoculation of trapped field mice with the bacteria, and the subsequent release of the diseased mice, as the best means of securing the spread of the disease.

The great objection to the use of such bacterial agents against rodents rests in the fact that the bacteria employed are so closely related to bacteria causing disease among man. The harmlessness of such bacteria to human beings is as yet unproved and outbreaks of disease among human beings have been attributed to the use of such bacterial cultures (51). Savage and Read (52) pointed out that rats infected with bacilli of the Gaertner group may serve as a means of infecting meat, thus being a possible cause of meat-poisoning outbreaks.

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" Polyhedral " Diseases. Closely related in many ways to the bacterial diseases are the so-called " polyhedral " diseases which attack many of the Lepidoptera. They are characterized by a " wilt " of the caterpillar and by the formation, in the bodies of the infected caterpillars, of polyhedral-shaped highly refractive granules. Glaser and Chapman (53) indicated the existence of several forms of polyhedra which they consider arise as a reaction against the invasion of a virus. Attempts to utilize practically the " Wipfel-krankheit " of the Nun Moth (*Lymantria monacha*) in Germany and the Wilt disease of the Gipsy Moth (*L. dispar*) in the United States have met with but indefinite success, although it is known that at times these infections contribute greatly towards the natural control of these two pests. It is questionable, however, whether, until more is known of the nature and methods of transmission of these diseases, attempts to utilize them as agents of insect control will be successful.

The possible use of a mild strain of a particular virus to combat more virulent strains has been discussed on p. 27. It is still per-missible to describe this phenomenon as an application of Biological

Control but, as with the polyhedral diseases, its successful application is dependent on a fuller knowledge of the nature and methods of transmission of these viruses.

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The Spread of Beneficial Fungi and Bacteria.

Considered as a method for biological control, the employment of beneficial bacteria differs from the employment of beneficial insects in that the results are not permanent. Once a beneficial insect is established in a suitable habitat, there is little work involved in its maintenance beyond the avoidance of practices detrimental to its development; its spread is automatic. With the bacteria and to a certain extent the fungi, though a severe infection may be established, the maintenance of the epidemic requires the presence of suitable conditions. Beneficial insects are more robust and are less sensitive to external conditions than the fungi or bacteria.

Further, the mechanism of the spread of the bacteria is often complex in character. There is good reason to believe that the fleas of rodents contribute to the propagation of the bacterial and virus diseases, just as do the various insect pests of human beings. The extent of spread of the disease organism is therefore dependent upon the relative numbers of the pest. It may also be that the more rapid passage from host to host renders the parasite increasingly virile until finally the epizootic breaks out. Once favourable conditions are established the disease becomes a potent factor in the reduction of the numbers of the pest and in the restoration of equilibrium, but the disease is ineffective in preventing the damage occasioned by the initial increase in the numbers of the pest.

This failing is common to the whole scheme of biological control. The principle has a subtlety which makes it more attractive scientifically than the bludgeon of chemical control methods but which may have tended to mask the fact that the successful examples of biological control, whether against insect pests or noxious weeds, have all involved a high initial degree of infestation. This point is illustrated by the examples of successful control selected by Sweetman (54) who also segregated cases where this high initial infestation has been reduced either to a level at which no serious loss is caused or at which the use of supplementary cultural, chemical or

mechanical control measures becomes practicable. In general it may be said that biological factors, though tending to maintain equilibrium, are unable to prevent the large increase in the numbers of the pest which is the preliminary to an outbreak. Only towards the end of the outbreak does the controlling influence of biological factors become of significant importance.

For this reason, the attention of entomologists appears to be turning more to the elucidation of the causes of the fluctuations in insect numbers. The epidemiological evidence indicates that the favourableness of the physical environment may be the predominant factor in the initiation of an outbreak. Consequently attention has been diverted from the biological factors to climatic and environmental factors in the study of the incidence of parasitism of crop plants.

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CHAPTER V

FUNGICIDES AND INSECTICIDES

The idea of applying a poisonous substance to the plant surface in order to kill the insect must have occurred to the first observers of the foliage damage caused by leaf-eating insects. Probably, too, in those cases where the fungus is visible on the plant surface, it was found that the application of certain materials would bring about the death of the pest. The early history of the use of insecticides and fungicides is therefore lost. It seems reasonable to suppose that a great variety of materials must have been tested in an empirical manner, a method by which were slowly sifted out many of the substances now in regular use as insecticides and fungicides.

Even if the insect were not killed by the treatment, various materials, such as decoctions of bitter or strong-smelling herbs, would be applied to the plant in the hope that the insect pest would be deterred or driven away by the objectionable taste or offensive odour. The realization that by the application of certain substances it is possible to protect the plant from fungus attack appears to date, however, from the accidental discovery by Millardet, in 1882, of the action of a lime-copper sulphate mixture. To-day, the function of a fungicide or insecticide is still either to kill the fungus or insect concerned, or to prevent the attack by a protective or deterrent action.

According to their mode of action it is thus possible to classify fungicides and insecticides into two groups : direct and protective. The direct or eradicative fungicides kill through contact with the fungus on the plant surface as in the case of lime sulphur used for the control of powdery mildews or of formaldehyde against Bunt of Wheat. The protective fungicide prevents the establishment of fungal infection as in the case of Bordeaux mixture against Potato Blight or of the organo-mercury derivatives against Stripe Disease of Barley. The distinction between direct and protective fungicides is emphasized because the principles underlying the use of the two types of fungicide differ. Firstly, it is essential that the protective fungicide be applied to the plant before infection is established,

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whereas the direct fungicide is applied to the infected plant. Secondly, factors relating to the retention of the fungicide upon the plant surface determine protective fungicidal efficiency, whereas direct fungicidal efficiency is more dependent upon complete contact between fungicide and fungus.

In the case of insecticides it is also convenient to differentiate between direct and protective insecticides. The direct insecticides are frequently called " contact poisons " and are used mainly against suctorial insects (see p. 30), killing by contact with and, probably, absorption through the body walls. In this group are also placed those materials which kill or inhibit the hatching of insect eggs, materials sometimes called " ovicides." The protective insecticides include materials effective against mandibulate insects which actually eat the surface tissues of the plant. Such insecticides are more commonly called " stomach poisons," for, when eaten with the plant tissue, they presumably kill the insect by absorption through the alimentary system. In so far as the efficiency of stomach poisons is related to the retention of the deposit upon the plant foliage, they may be regarded as protectant in character. Alternatively the presence of the insecticide may deter the insect from feeding, may interfere with the normal activities, e.g. egg-laying, of the pest, or may repel the insect by chemotropic action. In such cases the insecticide is essentially protectant in action.

This classification of insecticides and fungicides is quite arbitrary and it may be that a certain chemical will appear in more than one of the above categories. For example, nicotine, usually classed with the contact poisons, may act as a stomach poison or its presence may reduce attack by a deterrent action. The classification is nevertheless useful in that it enables generalizations to be made and affords a basis for the systematic discussion of the various groups of materials which find application as fungicides and insecticides. It is, however, convenient to separate for consideration those materials applied to the actual host plant from those applied to seed, the latter being discussed under Seed Treatment (pp. 260–274).

Proceeding therefore with generalizations concerning insecticides and fungicides applied to the growing plant, the toxic chemical must possess certain properties. Firstly, it must be effective in controlling the fungus or insect, or both, against which it is used without causing injury of economic importance to the host plant

or exerting too unfavourable an effect on its biological environment. The latter point, to which attention was recently drawn by Nicholson (1), is best explained by an example. Following the introduction of the tar oil washes for the destruction of insect eggs and lichens on fruit trees, infestation of the trees by Red Spider (*Oligonychus ulmi* Koch) became more noticeable. It was observed that the tar-oil wash, which has little effect on the eggs of this mite, killed its predators (2) such as *Anthocoris nemorum* L. It is also possible (3) that, by destroying lichen, the tar oil wash provides cleaner wood more favourable to the development of eggs of the mite with the result that tar oil spraying induces an improved biological environment for Red Spider. Fortunately suitable ways of overcoming this adverse effect of tar oil spraying are available, but it is evident, from the example, that the value of a chemical is not solely determined by its toxicity to the disease or pest concerned and by its non-toxicity to the host plant. These two considerations are, however, of primary importance and there must be a wide margin of safety between the concentration possessing effective insecticidal or fungicidal properties and that showing phytocidal properties. The sensitiveness of the plant to the insecticide or fungicide will, in general, vary with its stage of development ; the stomach poison or direct fungicide must cause no injury to foliage but, if the material is applied to kill insect eggs or hibernating insects upon the dormant tree, the question of foliage damage becomes less acute. A convenient distinction is often made between those materials applied during the period of active growth and those applied during the dormant season.

Secondly, it is necessary that the toxic material be amenable to application in an effective manner. The methods of application of insecticides and fungicides to the growing plant are conveniently classed on a physical basis thus :

I.   Spraying : when the toxic agent is applied in liquid form as a solution, suspension or emulsion ;

II. Dusting : when the material is applied in the form of a finely divided powder ;

III. Fumigating : when the chemical is applied in a gaseous form.

Of these three methods of application, the use of toxic gases and vapours is in many ways so different in practice to the use of dusts or sprays, that it is better to discuss the general features of the process later under the heading of Fumigants.

Spraying.

It is rarely that the active insecticide or fungicide is itself in a form convenient for application as a spray. Dilution with water, the cheapest and most available " carrier," is usually necessary, the spray being either an aqueous solution or, if the active ingredient is water-insoluble, a suspension or emulsion. In the case of suspensions and emulsions it is evident that such heterogenous systems should possess a stability sufficient to ensure the application, under practical conditions, of a dilution of uniform and known concentration of active constituent. To confer this stability, supplementary materials are often employed as constituents of sprays. Thus the sedimentation of the solid particles of a suspension may be delayed by the addition of protective colloids and dispersing agents, whilst the coalescence of the dispersed droplets of an emulsion may be retarded by the addition of suitable emulsifiers.

By the substitution of water as the carrier in sprays by liquids of lower surface tension, it is possible readily and cheaply to produce mists of droplets of extremely fine particle size. This greater degree of dispersion reduces the amount of spray required for effective distribution and it becomes an economic proposition to use carrier liquids such as kerosene. The active constituent is dissolved or emulsified in the kerosene which is then dispersed. When water is used as the carrier, dispersion is usually achieved by the passage of the spray under pressure through special nozzles, many of which have been described and discussed by Davies and Smyth-Homewood (4). With kerosene as the carrier an alternative method is possible in which the spray, not necessarily under pressure, is dispersed by the action of a copious current of air directed against a jet of the liquid. The energy necessary for dispersion is applied, in the first case, through the liquid, in the second case, through the air stream. To the second case the somewhat misleading term " atomization " is applied.

Dusting.

Dusting, the application of the toxic material in the form of a finely divided powder, has in certain districts almost superseded spraying, for it offers particular advantages from the grower's point of view. Whereas previously the use of dusts, as distinct from sprays, had been confined to isolated instances such as the employment of " flowers of sulphur " against hop " mould " (*Sphærotheca humuli*), many of the commoner fungicides and insecticides can

now be applied in powder form, the active material being diluted with a suitable " carrier."

The chief advantage of dusting over spraying is that by the use of a dust the factor of water supply vanishes. The expense of laying on a water supply, the necessity of transport of water, both in bulk or where the toxic material contains water, and the possibility that the water supply may fail, disappear. Secondly, the difficulties of preparation are reduced ; the dust may be purchased ready for application, dispensing with time and labour for the preparation of stock solutions and the cost of mixing vessels and platforms, whilst in cases of urgency the material is available without delay. Lastly, the apparatus employed being lighter than the water-carrying sprayers, the work and time involved in the application are reduced, and the method is more suitable for rough or hilly ground. This advantage of dusting is well illustrated by the use of aeroplanes for the application of dusts to forest trees when density of growth renders application from the ground impracticable.

On the other hand, it is by no means established that in all cases the control secured by dusting is as efficient as that obtained by spraying. Undoubtedly in some instances the reverse may hold : the light powder drifts better than the heavy spray, resulting in a better penetration into the underlying foliage. This lightness of the dust, however, makes it possible to apply the powder only when there is but little wind and spraying is frequently practicable under conditions when dusting is impossible. Again, the fine cloud produced by dusting may cause great inconvenience to the men employed in the work. Secondly, it is questionable whether the adherence of the dust deposit is in all cases as good as that of a spray deposit. It is often necessary to dust only when the foliage is wet with dew or rain in order to secure a satisfactory protective action.

Atomization shares the advantages and disadvantages of dusting. It is more convenient than spraying under conditions where the passage of heavy spray machinery is difficult, e.g. in brassica crops, but can be carried out only in calm weather. The peculiar merits of atomization are perhaps best utilized in the still conditions of the glasshouse where it enables the use of materials not sufficiently volatile for fumigation proper. Although still in the experimental stage, the drag-sheet device, by which the atomized or vaporized material is confined below a light impervious sheet dragged behind the atomizer, deserves mention (5) for it is applicable to the treat-

ment of ground crops such as strawberries or peas, crops which present special difficulties in spraying on account of their dense and low-growing habit.

Given a chemical of high toxicity and suitable methods for its application, the effectiveness or field performance of the spray or dust will depend on certain physicochemical properties which, though already mentioned, require further examination. The importance of completeness of contact, conveniently described as " coverage," which has been stressed in the case of direct insecticides and fungicides, reappears in the protective materials, for the uneven deposit will be a less efficient protection than that uniformly distributed. It may be advantageous to improve coverage by the addition to the spray of supplementary components usually termed " spreaders." Field performance is also dependent on the actual amount of toxic material which is retained on the sprayed or dusted surface. This amount, the spray residue, is determined by that initially retained and by the ability of the spray residue to withstand agencies, e.g. subsequent growth of the substratum, rain, wind, etc., tending to its removal, a quality which it is convenient to call " tenacity." It is again possible to add supplementary components, usually termed " stickers " to improve the retention of sprays and dusts. Finally, in the case of insecticides and fungicides not directly toxic themselves but from which, by various agencies, an active toxic product is formed after application, field performance will be governed by the inherent toxicity of the active derivative and the readiness with which lethal concentrations are liberated, i.e. the " availability."

Summarizing, the main requirements of a satisfactory spray or dust are :

(1) High field performance : determined by the
    (a) inherent toxicity and
    (b) availability of the active constituent : the
    (c) coverage and
    (d) initial retention of spray or dust and the
    (e) tenacity of the residue.
(2) Low phytocidal activity,
(3) stability of the concentrate in storage and a
(4) stability after dilution to spray strength, sufficient to ensure the application of a uniform known concentration of active constituents.

Items 1 (a), 1 (b) and 2 are characteristic of the particular insecti-

cide or fungicide employed and must be discussed specifically. Similarly, reference to supplementary spray materials used as " activators " to improve availability or as " correctives " to reduce phytocidal properties, must be reserved for particular treatment. But in the case of spreaders added to improve coverage, of stickers added to increase retention, of emulsifiers and protective colloids added to enhance stability, there are general points for discussion. It is therefore convenient to consider, somewhat out of order, the nature and action of these last four groups of supplementary agents.

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SPREADERS

The term " spreader " has been used to embrace all types of auxiliary spray materials (6) but it is advantageous to restrict the term to those materials which directly facilitate contact between spray and sprayed surface. It is a common experience that water falling as rain or dew on a cabbage leaf collects to large droplets which run off leaving the leaf surface dry. In other words, no stable liquid/solid interface is formed when water is applied to cabbage foliage. The function of a spreader is to promote the formation of the liquid/solid interface, maximum activity being attained when the air/solid interface disappears, i.e. when the spray covers the entire sprayed surface.

The Mode of Action of Spreaders.

It is convenient to differentiate, in the present state of knowledge concerning the mode of action of spreaders, between three properties upon which, in a gas/liquid/solid system, the extent of liquid/solid interface is dependent. The first may be termed the wetting properties of the liquid for the solid, which determine the extent of the liquid/solid interface when excess of liquid is drained from the solid surface. Thus the droplet of dew runs off leaving the cabbage leaf dry because the leaf is not wetted by water. The second method of formation of the liquid/solid interface is by the extension of the

liquid by capillary forces over the solid surface, a process which is best described as spreading. It is advantageous to retain the term " spreading " used by physicists for this phenomenon although, in spray practice, the term has the wider definition stated above. Thirdly, it is possible for the spray to possess the property of penetrating into the porous solid, a property of importance, for example, in the displacement of the air from the densely-packed conidiophores of a powdery mildew by a direct fungicide or, in the penetration by a contact insecticide, into the closely massed insects of a colony of Woolly Aphis.

The Comparison of Spreader Efficiencies.

Upon the basis of these three properties it is possible to consider methods of evaluating the efficiency of various spreaders.

(*a*) **Wetting Properties.** The criterion of wetting being the formation of a stable non-retreating liquid/solid interface when excess of the liquid is drained from the solid, it is evident that in the ideal case the liquid will remain as a persistent film over the solid. If wetting is not perfect, the liquid will retreat to form a droplet showing a definite angle between the surfaces of liquid and solid at the air/liquid/solid circle of contact. This angle is constant for any given liquid/solid system, and is called the receding contact angle, receding because the liquid is receding or retreating from the solid surface. Perfect wetting is attained when the receding contact angle is zero and this angle affords a measure of wetting properties.

The commonly used test of dipping a waxed card into the spray and observing that, on withdrawal, the liquid film does not retreat into droplets is, in fact, the observation that the receding contact angle of the spray on the waxed surface is zero. As such, the test is a simple method of assessing wetting properties for the waxed surface.

(*b*) **Spreading Properties.**—If spreading properties are defined as the ability of a liquid to spread over a solid, it would appear that they may be assessed by the comparison of the areas of spread of droplets of definite volume placed upon the solids under examination in a manner such that the area covered is determined solely by capillary activity. The use of area of spread as a criterion of spreading properties has been examined by Woodman (7), by O'Kane, Westgate, Glover and Lowry (8) and by Evans and Martin (9).

Theoretically the area of spread of the droplets will be determined by the three surface tensions involved. The surface tension of the liquid at the air/liquid interface, γ_1, and the interfacial tension at the liquid/solid interface $\gamma_{1,2}$ will oppose, whereas the solid/air tension γ_2 will favour, the extension of the droplet over the solid. If the latter force is greater than the sum of the other two, i.e. if

$$\gamma_2 > \gamma_1 + \gamma_{1,2} \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad (1)$$

the droplet will spread. It is evident from this equation that the smaller the surface tension the more likelihood of spread. Surface tension was used by Woodman (6) for the evaluation of spray spreaders, but, as spreading properties are dependent on the three surface tensions involved, the method has met with little success. As no methods are known for the determination of the solid and interfacial tensions γ_2 and $\gamma_{1,2}$ Cooper and Nuttall (10) employed a thick oil in place of solid which enabled them to evaluate the " spreading coefficient " :

$$\text{S.C.} = \gamma_2 - (\gamma_1 + \gamma_{1,2}) \qquad \cdot \qquad \cdot \qquad \cdot \qquad (2)$$

a procedure extensively used by Cupples (11).

It has been shown that, in a drop of liquid resting on a plane surface, the angle within the liquid between the liquid and solid surfaces at the air/liquid/solid circle of contact is a constant independent of the volume of the droplet. This angle, designated the advancing contact angle θ_a,—for the liquid, in contradistinction to the case of wetting, is advancing over the solid—is related to the three interfacial tensions involved by the following equation :

$$\gamma_2 = \gamma_1 \cos \theta_a + \gamma_{1,2} \qquad \cdot \qquad \cdot \qquad \cdot \qquad (3)$$

As the contact angle can be determined experimentally, attempts have been made to utilize it as an index of spreading properties notably by Stellwaag (12), English (13), and by O'Kane *et al* (8).

Combining equations (2) and (3), an alternative expression of the " spreading coefficient " is obtained :

$$\text{S.C.} = \gamma_1(\cos \theta - 1) \qquad \cdot \qquad \cdot \qquad \cdot \qquad (4)$$

which was employed by Wilcoxon and Hartzell (14) as a measure of spreading properties.

Present evidence suggests that all the proposed methods, with the exception of those based only on the single surface tension γ_1, provide a useful indication of the spray performance of a particular spreader, for high degrees of correlation were obtained by Evans and Martin (9) between various pairs of methods. Mack

(15) obtained satisfactory agreement between area of spread and contact angle but found that only small droplets assume the advancing contact angle, larger droplets exhibiting a fluctuating angle intermediate between the advancing and receding angle. Hoskins and his co-workers (16) suggested that the above-mentioned methods might not provide useful information of spray performance for the two following reasons. Firstly, the final equilibrium values for surface phenomena of solutions are not usually attained immediately the surface is formed. Only when equilibrium is established between the surface and bulk concentrations of the surface-active component, for example, does the surface tension reach a steady reproducible value. Laboratory assessments based upon such final static values may therefore give inadequate information of the dynamic value coming into play when the solution is sprayed. Secondly, the frictional electrostatic phenomena occurring when the liquid is broken into droplets by the spray appliance and when the droplets meet the surface may affect performance. Actually Wampler and Hoskins (17) were unable to trace any relationship between performance and electrostatic phenomena while Martin (18) established significant correlations between assessment of wetting and spreading properties based on spray performance and on contact angle estimates.

(c) **Penetrating Properties.** Theoretically the ability of a liquid to enter a tube of radius r is given by the expression :

$$P_c = \frac{2\gamma_1 \cos \theta_a}{r} . \qquad . \qquad . \qquad . \qquad (5)$$

in which θ_a is the advancing contact angle. It may therefore be assumed that penetrating properties will be proportional to the product $\gamma_1 \cos \theta_a$. In practice, however, it is probable, in view of the rapid evaporation of the spray after application, that the rate of penetration is also of importance. The rate of penetration into a given porous solid will be inversely proportional to the absolute viscosity of the spray. Hoskins (19) demonstrated that the rate of penetration of a number of insecticidal oils was proportional to surface tension divided by viscosity. It is probable that the oils he examined exhibited a low advancing contact angle upon the solids used, but, with aqueous solutions which have, in general, a higher advancing contact angle, this factor must receive consideration.

A simple laboratory assessment of penetration properties is obtained from time of sinking tests, in which the time is taken

for the submergence of cotton-wool or of hanks of unbleached cotton placed on the surface of the spray. But as the theoretical basis of this test is still obscure it is better to rely on comparisons based on equation (5) or on biological tests of the types used by Greenslade (20), or by Kearns, Marsh and Martin (21). In such tests a standard concentration of a non-volatile active constituent is used, only the penetrant differing in the series of sprays. The test organism should be chosen from those in the killing of which penetration is known to be required, due allowance being made for the effect, on toxicity, of factors other than penetration.

As the precise relative importance of wetting, spreading and penetrating properties in determining the efficiency of spray spreaders is governed to some extent by the nature and purpose of the active constituents with which they are used, a general conclusion regarding the merits of particular methods of their evaluation may be misleading. Further attention is given to this problem in the discussion of the action and efficiency of " stickers " (p. 92).

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The Classification of Spray Spreaders.

Reverting to the practical definition of a spray spreader as a material imparting to the spray better wetting, spreading or penetrating properties than those of water alone, it is possible to classify

spreaders into two groups, water-soluble and water-insoluble. The latter group is represented by the oils, a general term which includes the mineral or hydrocarbon oils, glyceride or fatty oils, and various terpene oils such as the pine oils.

Oils as Spreaders. Although the high spreading efficiency of oils has long been known, the observation that oils can function, *per se*, as satisfactory carriers of insecticides is of recent date. The belated recognition of this property may be due to the fact that previously trials had been made only with oil emulsions containing water-soluble emulsifiers themselves effective spreaders. The high insecticidal efficiency of cottonseed oil-pyrethrum-soap emulsions, for example, would have been associated with the excellent spreading properties of the soap. Austin, Jary and Martin (22) demonstrated that cottonseed oil emulsified with Bordeaux mixture, an emulsifier of inferior spreading properties, was an effective carrier of nicotine, an efficiency which is to be associated with the excellent spreading properties of cottonseed oil.

The penetrating properties of oils, investigated as has been mentioned above by Hoskins (19), appear to be more marked than those of water-soluble spreaders. De Ong, Knight and Chamberlin (23) showed the penetration of the tracheæ of Red Scale by oils and oil emulsions, and the penetration of oils into plant tissue has been repeatedly demonstrated in investigations of the phytocidal activity of petroleum oils (see p. 204). In this connection, de Ong (24) has suggested that improved fungicidal efficiency might be obtained by the use of oil-soluble fungicides and has advanced evidence of the penetration of copper resinate dissolved in pine oil into leaf tissue.

A disadvantage of oils as spreaders is that their applicability is presumably limited to oil-soluble toxic constituents.

Water-soluble Spreaders. Spreading properties are, in general, a manifestation of surface activity which is the result of the peculiar property possessed by certain water-soluble compounds of lowering the surface tension of water. Gibbs (25) has shown by thermodynamic reasoning that when the surface tension of a liquid is lowered by the addition of a solution, the solute is more concentrated at the surface layer, i.e. the solute is surface adsorbed.

The phenomenon of surface adsorption is exhibited markedly by compounds possessing a particular type of molecular structure, namely, a bulky molecule itself not water-soluble but which is rendered miscible with water by the presence of certain water-soluble or " polar " groups. Such molecules (or ions) are con-

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veniently described by Hartley (26) as amphipathic, one end of the molecule being water-attracting (having a sympathy for water), the other end being water-repelling (having an antipathy for water). This relationship between chemical structure and surface adsorption was put forward by Langmuir (27) and Harkins (28) who demonstrated that surface adsorption is accompanied by an orientation of the molecules of the capillary-active compound at the surface. The non-polar group of the molecule is directed away from the water modifying the surface properties of the solution.

The conception of amphipathy has assisted the synthesis of many compounds of potential value as spray spreaders, but so large is their number that all which have been employed as such cannot be mentioned. The idea also forms a convenient basis for the classification of the water-soluble spreaders and, as the simpler are surveyed, its application to synthesis will become apparent.

For primary classification, the character of the non-polar part of the molecule may be used according to whether it be (i) long-chain (or alkyl), (ii) cyclic or (iii) undetermined.

(i) LONG-CHAIN DERIVATIVES.

Soaps. In 1821, at a time before the nature of the disease was known, Robertson (29) recommended the use of sulphur for the treatment of mildew on peaches : " It should be mixed with soap-suds and then applied by dashing it violently against the tree . . . by means of a rose syringe." The soap, in this case, functions not only as a spray spreader, but also as a wetter for sulphur, the particles of which are not readily wetted by water alone.

All soaps are of similar chemical structure, for they are the alkali salts of the fatty acids, the carboxylic acid derivatives of long-chain hydrocarbons. Surface activity appears to any marked extent only when the carbon chain exceeds a certain length, about C_{12}, thus forming the preponderant non-polar group, the polar group being the carboxyl (–COOH) group of which the hydrogen is replaced by the appropriate alkali. For practical purposes it is sufficient to assess the value of a particular soap sample as a spray spreader on the basis of its content of combined fatty acids (30).

Soaps have serious drawbacks as spray spreaders. Firstly, as soaps of the non-alkaline metals are insoluble, the alkali soaps are precipitated as curd by hard water and by the more important protective insecticides and fungicides, e.g. lime sulphur, Bordeaux mixture, calcium or lead arsenate. Secondly, soaps are difficultly

soluble in cold water. For this reason the soaps most generally used in spray practice are the soft soaps, i.e. the potassium soaps in contradistinction to the hard sodium soaps of general household use. Even with soft soaps it is necessary to use hot water for the preparation of stock solutions suitable for dilution to spray strength. This troublesome procedure may be avoided by the cold-water method of preparing soap solutions, recommended by Martin (31), in which a fatty acid liquid at ordinary temperatures, e.g. oleic acid, is added to a dilute solution of caustic soda to form sodium oleate :

$$CH_3.(CH_2)_7.CH : CH.(CH_2)_7COONa.$$
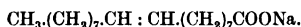
In place of the alkalies, various organic bases have been suggested for soap preparation. One such compound, tri-β-hydroxyethyl-lamine $(CH_2.CH_2OH)_3N$, is the active constituent of **Triethanol-amine,** which has been recommended for emulsifier purposes (32). But the soaps of the organic bases are precipitated by calcium salts and a more drastic alteration to the molecule is necessary to avoid this disadvantage, as exemplified by the next group :

Sulphonated Oils.—The treatment of certain fatty oils, not with alkali as in the production of soaps, but by sulphuric acid or other sulphonating agents, leads to the introduction of the polar $-SO_3H$ group. Turkey Red oils, for example, are produced by the sulphonation of castor oil, a treatment which confers water solubility and surface activity to the glyceride. Turkey Red oils, however, still form relatively insoluble calcium salts, but it has been shown that, by more drastic sulphonation, it is possible to produce sulphonated oils of which the calcium salts are sufficiently soluble for the purpose required. This difference in solubility is associated with the fact that the Turkey Red oils are readily hydrolysed by dilute acid which splits off the SO_3H group as sulphate. These compounds may therefore be regarded as sulphuric acid esters, and are more accurately described as " sulphated " oils containing the group $-C-O-SO_3H$. Drastic sulphonation introduces the true sulphonic acid group, $-C-SO_3H$, in which the sulphur atom is directly combined with the carbon atom, a bond not readily broken by hydrolysis. The true sulphonated oils have as yet found no widespread application as spray spreaders, but among the older type of sulphonated glycerides are most useful emulsifying agents.

The attachment of the sulphate or sulphonate group to the fatty acids as distinct from the glycerides presents difficulties which may

be avoided in a variety of ways illustrated from the sulphated alcohols and the Igepons.

Sulphated Alcohols (*sodium alkyl sulphates*). The only common naturally occurring fatty alcohol is cetyl (hexadecyl) alcohol, $C_{16}H_{33}OH$. Sulphated cetyl alcohol or, to use its proper chemical name, sodium cetyl sulphate, $C_{16}H_{33}OSO_3Na$, is the active constituent of a number of proprietary detergents but, because of the poor solubility in cold water of itself and its calcium derivative, it is not satisfactory as a spray spreader. The substitution, in place of cetyl alcohol, of lauryl (dodecyl) alcohol, $C_{12}H_{25}OH$, yields a sulphate of more ready solubility in cold water. Dodecyl alcohol is the main constituent of a proprietary product Lorol, made by the hydrogenation of coconut oil or fatty acids. Sulphation of this product yields **Sulphonated Lorol** (33) and the same active ingredient appears in other proprietary products e.g. **Dreft, Dupenol M.E., Gardinol W.A.** (34) and **Orvus**.

A second source of the long-chain alkyl sulphates is the petroleum industry, in particular, in the removal of olefines by absorption in sulphuric acid. The sodium alkyl sulphates, produced by the neutralization of the acids with sodium hydroxide, are secondary alcohol sulphates, for the sulphate group is attached to an intermediate carbon, thus giving a compound with two alkyl tails, $R'(R'')CH.O.SO_3Na$ as distinct from the primary alcohol sulphates $R.CH_2O.SO_3Na$ described in the previous paragraph. Proprietary products based on the secondary alcohol sulphates include the **Ester Salts** marketed by the Shell combine and the **Tergitols** (35) of the Carbide and Carbon Chemicals Corporation.

Igepons. As their name implies this group was elaborated by the I.G. Farbenindustrie, and in them the attachment of the sulphonic acid group to fatty acid is achieved by the use of a short bridging group, as in **Igepon A** :

$$CH_3(CH_2)_7.CH:CH(CH_2)_7.CO.O.CH_2CH_2.SO_3Na.$$
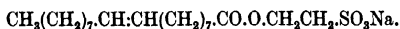
This compound, which may be regarded as an oleyl ester of isethionic acid, is unstable in alkaline solution, a disadvantage not shared by **Igepon T**, which is a corresponding taurine derivative :

$$CH_3(CH_2)_7CH_2:CH_2(CH_2)_7.CO.N(CH_3).CH_2CH_2.SO_3Na.$$
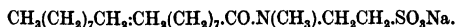
The Igepons appear as the active constituents of certain proprietary spray spreaders of undeclared composition marketed in this country.

The carboxylate, sulphonate and sulphate by no means exhaust

the available polar groups, but it is now necessary to pass to an extreme type :

Sapamines. Hartmann and Kagi (36) found that certain substituted ethylene diamines combine with oleic acid to form a base soluble in dilute acids yielding surface-active salts. These derivatives have been placed on the market under the name Sapamine : **Sapamine CH**, which is the hydrochloride of this base,

$$CH_3(CH_2)_7.CH:CH(CH_2)_7.CO.NH.CH_2.CH_2.NH(C_2H_5)_2Cl,$$

is decomposed by alkalis, a difficulty overcome by conversion of the base to a quaternary ammonium salt as in **Sapamine MS.** The Sapamines appear as spray spreaders in certain proprietary fungicides employed on the Continent.

There are structural resemblances between the Sapamines and Igepon T, but an important difference is that whereas in Igepon T the long oleyl chain is in the anion, in the Sapamine it is in the cation. The Sapamines may therefore be called " reversed soaps " and are indeed precipitated by soaps as well as by other long-chain anions.

Quaternary Ammonium Derivatives. The employment of the quaternary ammonium salt, as in the Sapamines, is a simple way of introducing the required polar group adopted in many synthetic textile assistants. Greenslade (20) for example, referred to a product, RD 4117, which is presumably a member of this group and of the general formula $R-N(R_1)_3Y$ in which R is a long alkyl chain, R_1 a short radical and Y a salt-forming group. Compounds of particular interest to the entomologist arise when insecticidal nitrogenous derivatives such as nicotine are substituted for ammonia in this type of product. Thus **Tinocine D**, which contains a long-chain nicotinium bromide, was found by Austin, Jary and Martin (22) to possess not only excellent spreading but also good insecticidal properties.

The present tendency in the synthesis of surface-active compounds is away from the simple structure of a long hydrocarbon chain terminated by a polar group exemplified by the above mentioned compounds for, in them, it is found that, if the hydrocarbon group is bulky enough to ensure detergent efficiency at temperatures near boiling, activity at the lower temperatures of sprays is small. One method of avoiding this disadvantage is to render the hydrocarbon group less regular by the introduction of subsidiary polar groups, e.g. the ethylenic linkage –C:C– as in oleic acid, by branching the

chain, or by incorporating aromatic groups, thus combining the long-chain and cyclic structures. The latter group must, however, be next considered.

(ii) SPREADERS OF CYCLIC STRUCTURE.

It is convenient to begin with the earlier non-synthetic materials, among the first of which are :

Resinates. Commercial resinates are prepared by treating resin (colophony) with alkali, the predominant constituent being the alkali abietate. Abietic acid has a complicated ring structure, the polar groups being carboxyl and hydroxyl groups. They have long been employed for the adulteration of true soaps and it is therefore required, in this country (30), that the percentage of resin acids of samples of soft soaps for spraying purposes shall be declared.

Like the soaps the resinates are precipitated by hard water and by soluble salts of metals other than the alkali metals. This disadvantage may be overcome by sulphonation, and **Neopen SS,** which is stated to be a sulphonated abietene, has been used as a wetting agent in spray residue removal (37). The sulphonation products of terpene alcohols, constituents of the distillate of which resin is the residue, form the active constituents of **Emol,** a spreader introduced in France (38).

Naphthenates. Interesting groups of surface-active compounds are to be found among the products of petroleum refinement. The naphthenic acids are naturally-occurring petroleum acids extracted from crude oil by alkali treatment. Martin (39) examined their potential value as spray spreaders, but concluded that phytocidal properties, associated with the crude oil present as impurity and possibly inherent in the refined naphthenates, rendered them of doubtful value. Further, as the calcium naphthenates are insoluble, they would be unsuitable for use with the majority of insecticides and fungicides, a disadvantage not shown by certain of the petroleum sulphonic acids.

Petroleum sulphonic acids. In the refinement of petroleum oils, in particular the lubricating and high-boiling oils, with sulphuric acid, petroleum sulphonic acids are formed which have been classified by Pilat and his colleagues (40) on the basis of solubility relationships of the calcium salts. Sulphonic acids yielding calcium salts insoluble in water and in ether were called alpha-acids, those of which the calcium salts were soluble in ether but insoluble in water

were the beta-acids, and those yielding calcium salts insoluble in ether but soluble in water were termed the gamma-acids.

Martin (39) showed that the majority of commercial soap substitutes derived from petroleum and marketed under such names as "Naphthenic sulpho-acids," or petroleum soaps, contained the beta-sulphonates as the main surface-active ingredients. These materials are produced by the alkali treatment of the refined oil in which the beta-sulphonic acids are soluble and appear after sulphuric acid treatment. "Kontakt," recommended in Russia (41) for use with nicotine washes, probably contains beta-sulphonates, but the usefulness of these materials as spray spreaders is limited by their precipitation by soluble calcium salts.

The gamma-sulphonates, which forming soluble calcium salts are suitable for use in a wider range of sprays, appear in the sulphuric acid layer from oil refinement. Pilat and Sereda (B.P. 343,530) and Martin (39) describe methods for the isolation of the crude calcium gamma-sulphonates, which have been found satisfactory spray spreaders (42).

"Penetrol," which has been recommended in the United States (43, 44) particularly as a spreader for use in nicotine washes, is stated to contain the sulphonation products of "oxidized" petroleum oil as active constituents. Martin (39) found that the sample examined was a miscible oil preparation of fuel oil containing sulphated material as emulsifier. This material, which gave soluble calcium salts of strong surface-active properties, was decomposed by acid, indicating that, in contradistinction to the gamma-sulphonates, it was of the sulphuric acid ester and not a true sulphonate.

The introduction of aliphatic chains into cyclic petroleum sulphonic acids is the basis of the active constituents of the proprietary wetting-out agent **Agral N** (B.P. 274,611).

Aromatic derivatives. Of the simple aromatic compounds, α- and β-naphthols, the monohydroxy derivatives of naphthalene were found by Martin and Salmon (45) to wet powdery patches of the mildew *Sphærotheca humuli* when applied as sodium naphtholates at concentrations toxic to the mildew. The polar group is, in these compounds, the hydroxyl group, naphthalene forming the bulky non-polar group. Substitution of the hydroxyl by the sulphonic acid group yields the naphthalene sulphonic acids, and it has been claimed that the introduction of lower alkyl groups into the naphthalene sulphonic acids increases markedly their surface activity. A wide range of proprietary products, e.g., Nekals, Alkanols, Vatsol,

Invadines, etc., have as their active constituents the iso-propyl and butyl naphthalene sulphonates, which are characterized by the ready solubility of their metallic salts.   Of these products **Agral 2** has been subjected to spray trials and certain **Alkanols** and **Vatsol** have been used for spray residue removal (37).   **Lethalate Wetting Preparation** (B.P. 429,615), among the first of the synthetic soap substitutes to be applied for spraying purposes (46), is compounded of sodium " lorol " sulphate and di-isopropyl naphthalene sulphonates.

The device of irregular non-polar residues, mentioned above in the discussion of the long-chain surface-active components, has been used in the cyclic series.   Examples are the series of sulphonated phenyl derivatives described by Ginsburg (47), namely, **Arescap** (the monosodium sulphonate of butyl phenyl phenol) and **Aresket** (a sulphonated alkylated diphenyl).   One advantage of these two compounds is their solubility in organic solvents which renders them useful in the compounding of self-dispersing liquids.   Extreme examples (B.P. 479,835 and 479,897–9) are of the structure in which $(R_1)_n.X.B.R_2$— is the non-polar residue, R_1 representing alkyl groups attached to a cyclic group X. B being an interrupting group serving for the attachment of another alkyl group R_2 to which is linked the main polar group which may be the sulphonate, sulphate, phosphate or thiosulphate.   Compounds covered by the latter patents represent the most complex, to date, of the synthetic cyclic spreaders.

This complexity still falls short of that of the miscellaneous non-synthetic spreaders which remain for discussion.   Indeed the structure of the majority is incompletely known, but all are cyclic derivatives.

Bile salts.   The high surface activity of bile salts has long been known, but the commercial preparations known as sodium tauroglycocholate are too expensive for use as spray spreaders. **Adhésol,** which has been used on the Continent mainly with Bordeaux mixture (48), is stated to be a preparation of ox bile (49). Chemically the bile salts are the sodium salts of glycocholic and taurocholic acids, the latter being the condensation product of cholic acid, of complex ring structure, and taurine, aminoethanesulphonic acid.   It therefore resembles Igepon T in the nature and method of attachment of the polar group.

Sulphite lye.   This product is derived from the manufacture of cellulose from wood pulp.   In the sulphite process, the pulp is

digested with sulphur dioxide in the presence of lime or caustic soda, whereby the lignins are rendered soluble and pass into the lye. The waste lye, which is too rich in sugars and other organic matter to be discarded as an effluent, is concentrated or is fermented to yield alcohol prior to concentration. The concentrated product is available either as a thick syrup or as a powder, and is known as sulphite cellulose lye, lignin pitch, Goulac, Banderine, Bindex, etc. The syrup, if of specific gravity not greater than 1·3 (60° Tw.), is easy to measure and to mix with water, though it is less convenient to transport than powder forms. Certain types of powder, in particular those of soda base, are, however, highly deliquescent and unsuitable for recommendation to growers. Powdered sulphite lyes of a non-deliquescent character are widely used in this country as a constituent of proprietary spray spreaders.

The use of sulphite lye as a spray spreader was suggested by Martin (39) and its practical value demonstrated by spray trials (42, 50). In the critical studies by Evans and Martin (9) it was shown that the soda base sample used owed its properties to its activity as a wetter, the spreading properties (in the limited sense) of the solution being little better than those of water. Sulphite lye has also proved of value as an emulsifier (46) and protective colloid, its great advantages being cheapness and the wide range of spray materials with which it can be used.

On the other hand, little is known of the chemical character of its active constituents and chemical standardization is not yet possible. Hibbert and his colleagues (51) showed the presence of lignosulphonic acids and attention may be drawn to the work of Howard (52) which suggests that a more complete isolation of the surface-active constituents, at least of the lime base material, may become a commercial possibility.

(iii) SPREADERS OF UNDETERMINED STRUCTURE.

Among spray spreaders of which the molecular structure is still not definitely known, certain protein derivatives are of importance.

Casein. Vermorel and Dantony (53) proposed the use of casein, which is the albuminoid separated from skim milk by the addition of rennet or acids, as a spreader for Bordeaux mixture. The material, in various forms, has since been widely used as a spreader for other spray materials to which soap cannot be added.

Casein, although insoluble in water, is readily dispersable if mixed with solutions of alkaline reaction. Thus the **Lime Caseins,**

sometimes called calcium caseinates, are intimate mixtures of hydrated lime and casein. The " **soluble caseins** " are produced by dissolving casein in strong, hot solutions of alkali, borax (the sodium salt of hypoboric acid, $Na_2B_4O_7. 10 H_2O$) or disodium hydrogen phosphate ($Na_2HPO_4. 12 H_2O$) and are probably degradation products. The direct use of **skim milk** was advocated by Robinson (54) who suggested the addition of the milk to water in the spray tank, followed by hydrated lime which neutralizes the acidity of the milk ; the toxic spray materials he added last.

Casein, being a protein, is of high molecular weight, the polar groups present being the amino and carboxylic radicals. The degradation products present in the soluble " caseins " are probably amino-acid derivatives of high molecular weight.

Gelatine. The first records of the use of the gelatine as a spray spreader are by David (55) and by Millardet and David (56), who investigated its use with Bordeaux mixture. Although not securing the popularity of lime casein, its use as a spray auxiliary has been urged, particularly with lead arsenate. Its advantages depend not so much on its properties as a wetter or spreader but its high activity as a protective colloid and as a sticker of the adhesive type. As the purified grades of gelatine are expensive, the cheaper and impure grades, such as glue or size, are used. Woodman (57) indicated that fish glues, which are soluble in cold water, may be less effective than other forms of glue as " stickers."

Saponin. The saponins form a group of glucosides, chemicals which by hydrolysis or by the action of specific enzymes yield sugars and other compounds of a non-carbohydrate character, the sapogenins. The saponins were early distinguished by their property of dissolving in water to form clear solutions which froth well on agitation. For this reason, it has been the practice to add certain of the saponins to carbonated beverages to improve their foaming qualities, whilst they have been employed for the production of foam in certain fire-extinguishers. The utilization of saponins for spraying purposes appears to have been first made by Bedford and Pickering (58).

Saponins are present in varying amounts in a wide variety of plants (see 59), but the more important sources of commercial saponin are the inner layers of the bark of *Quillaja saponaria* Molina (Soap bark), and the pericarp of the fruit of *Sapindus utilis*. The cost of extraction renders the price of the pure saponins prohibitive for commercial spraying practice, for which reason Bedford and

Pickering recommended the use of ground Quillaja bark, whilst Gastine (60) advocated the use of the powdered fruits of *Sapindus utilis*, a tree common in Algeria. There are, at the present time, a number of saponin preparations on the market at a price more suitable for practical employment, whilst the purer powders are of great use in experimental work.

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STICKERS

It is so evident that the efficiency of a protective spray or dust will depend on its actual amount on the surface to be protected that it is surprising that the physico-chemical properties affecting spray retention have only recently received study. Apart from the earlier work of Smith (61) dealing specifically with the deposition of lead arsenate, general studies were first initiated by Hoskins and Martin with their respective co-workers. So recent is this work that the terminology has not yet crystallized, hence it is necessary first to define the various terms used.

The amount of spray residue is determined by the amount initially retained and by its tenacity (see p. 75). It is probable that the American expression " sticker " was originally given to materials added to improve tenacity only, but it is now convenient to apply the term more generally to substances improving spray retention.

Considering first initial retention, this amount will depend on the maximum quantity of spray or dust that the surface can hold, and in the case of the application of amounts insufficient to give this full load, on the proportion of the spray or dust applied which is retained by the surface. Maximum initial retention is more clearly defined in the case of sprays, but the problem is here complicated, for only rarely are simple homogenous solutions used in spray practice. In most cases the sprays are the heterogenous suspensions and emulsions of which one component may be retained to a greater extent than other components. De Ong, Knight and Chamberlin (62), for example, found that the percentage of oil in certain emulsions draining from sprayed foliage was lower than that of the emulsion before spraying, indicating a preferential retention of the oil phase. Smith (63) in studying this phenomenon applied the terms " initial deposit " to the oil which, apparently, is deposited on the surface the instant the spray strikes the surface and " secondary deposit " to the oil deposited as a result of evaporation of the water in the droplets or film of spray. Hoskins and his colleagues (64, 65) used the terms " primary " and " secondary

deposits " for these two quantities, but it appears safer to adopt terms which do not imply the time sequence of deposition. Of such terms " preferential retention " used by Fajans and Martin (66) is preferred to " build-up " used by Marshall (67) to indicate the continuous increase of deposit with prolonged application of spray.

The example of the drop of dew rolling off the cabbage leaf indicates that the initial retention of sprays is dependent upon wetting properties, and the proportion of applied spray which is retained will increase with the wetting properties of the spray. But with present machinery intended for the application of copious amounts of spray under high pressure, the maximum initial retention is a factor of greater practical importance than the proportion of applied spray retained. Maximum initial retention (M.I.R.) in the case of simple homogenous solutions, was shown by Martin (68) to be a function of wetting and spreading properties, decreasing with improvement in these properties in accordance with the equation

$$\text{M.I.R.} = \sqrt{\gamma_1(1 - \cos\theta)} . \qquad . \qquad . \qquad . \qquad (6)$$

It was not possible to judge from the correlation co-efficients obtained whether the contact angle concerned is the receding contact angle (i.e. wetting properties) or the equilibrium angle intermediate between the advancing angles (spreading properties) and the receding contact angle. Practical considerations hint that, as the performance of the sprayed droplet is influenced by its kinetic energy, the receding angle is concerned in the case of the droplet which directly hits the surface.

Given a zero receding contact angle no part of the surface is left unwetted by the spray and " film coverage " (61) occurs. Theoretically the spray load would drain to a monomolecular film, but evaporation intervenes and the initial retention is determined by rate of evaporation and viscosity. The relationship between viscosity and the maximum initial retention of a spray completely wetting the surface was demonstrated by Woodman (69). Given imperfect wetting, droplets accumulate on the sprayed surface until coalescence and run off occurs. Evans and Martin (70) showed that maximum initial retention occurs at the point of incipient run off.

If a heterogenous emulsion or suspension is sprayed, preferential retention may occur with consequent increase in the spray load of the

preferred component beyond the quantity indicated by the maximum initial retention of the spray. The properties required for preferential retention to occur are obscure and Fajans and Martin (66) were unable to demonstrate its occurrence in the case of simple suspensions. In the case of emulsions, de Ong, Knight and Chamberlin (62) found that preferential retention of the oil phase increased with decrease in the stability of the emulsion as indicated by emulsifier content. Smith (63) suggested that the wetting properties of the aqueous phase of the emulsion also affect preferential retention, a view examined by Hoskins and his colleagues (64, 65). A slight improvement of wetting properties of the aqueous phase favours preferential retention but excessive wetting by this phase, generally accompanied by an increase in the stability of the emulsion, retards preferential retention presumably by inhibiting contact between the oil phase and the surface. This hypothesis does not appear to furnish a complete answer to the problem, for Fajans and Martin (71) were unable always to reduce preferential retention by the improvement of wetting properties without marked increase of emulsion stability.

If conditions are such that preferential retention of the oil phase occurs, this property can be used to enhance the retention of solids suspended in the emulsion (71). To obtain this effect the solid and emulsifier must be so chosen that an interaction, probably of chemical character, occurs resulting in a partial or complete adsorption of the oil phase by the solid. This phenomenon was also described by Marshall (67) who referred to the process as "inversion," for the suspended solid originally wetted by the aqueous phase becomes wetted by oil. This choice of term is unfortunate if it leads to confusion with the inversion of an emulsion (see p. 100). Oil-flocculation seems better and it is probable that the oil-flocculated solid performs analogously to the oil and that conditions determining preferential retention are similar in the two systems. The extent to which preferential retention of oil or of oil-flocculated solid can be used in practice to augment spray loads is dependent on the spray machinery available. The unstable character of the spray systems showing preferential retention demands good agitation in the spray tank and alert attention by the spray gang, requirements which would render such sprays unpopular except among more enlightened growers. Fajans and Martin (71), indeed, questioned the practicability of recommending sprays showing marked oil-flocculation for the present types of spray machines but, with

improved appliances, the phenomenon could be made of great practical use. Groves, Marshall and Fallscheer (72) have devised an injector type of sprayer for the application of oil-flocculated suspensions.

Turning now to factors affecting the tenacity of spray residues, it is a general rule that the finer the particles the more tenacious the deposit. Coarse particles of sulphur, for example, are rapidly removed by rain or wind. Similarly if the spray is of poor wetting properties it leaves large droplets evaporating to thick blobs of deposit easily removed. For this reason it was generally recommended that the early protective sprays, such as Bordeaux mixture, of poor wetting qualities should be applied in a fine mist-like spray in amounts just insufficient to cause drip from the foliage. The addition of spreaders, by improving coverage, tends to enhance tenacity and many of the older spray spreaders such as lime casein or gelatine can be classed as stickers. This effect is, however, offset firstly by the reduction of maximum initial retention following perfect wetting and, secondly, by the influence of the spreader upon the rain-resisting qualities of the spray deposit.

In most climates rain and dew are the main agents reducing spray residues and, as a general rule, Fajans and Martin (66) found that resistance to leaching is determined by the relative ease of wetting of the spray deposit. Thus spray spreaders which remain in the spray deposit in a form readily soluble in cold water, such as sulphite lye or certain of the synthetic spreaders, reduce tenacity whereas those difficultly soluble, such as gelatine, or which decompose on drying to insoluble products (e.g. lime casein) enhance tenacity. It is perhaps a rain-proofing action which renders the oils of special merit as stickers though the improvement of tenacity which they effect may be offset by the wetting properties of the emulsifier present. Fajans and Martin (71) showed, for example, that the adverse effect of sulphite lye, when employed at high concentrations as emulsifier, may outweigh the favourable effect on tenacity of oils. Of the oils they found cottonseed oil to be a better sticker than refined petroleum oil, a property perhaps associated with the semi-drying character of the former, which acts not only as a water-proofer but as an adhesive.

The idea of gumming the spray residue to the foliage forms the basis of many stickers. Flour paste, gums, dextrines (British gum) and, more recently (73), soya-bean flour have all been prepared and used. So efficient is flour paste as a sticker that Parker (74)

found it effective against Red Spider, *Tetranychus bimaculatus* Harv., not because it is directly toxic to this organism, but because it sticks it to the leaf.

Yet another factor which may influence tenacity is the effect of electrostatic charges. Wet leaf surfaces acquire a negative charge, the particles of a suspension or emulsion possess electrostatic charges, while the passage of the spray through spray nozzles or the impact of spray droplet with leaf induces frictional electrical charges. Moore (75) therefore suggested that a spray containing particles bearing a positive charge should yield a more tenacious deposit than one containing negatively-charged particles, since the former would be attached to the leaf surface whereas the latter would be repelled. He was able to show that the adherence of the ferric arsenate spray, of which the particles are positively-charged, is superior to that of the negatively-charged particles of the more usual arsenicals such as lead arsenate. These ideas have been critically examined by Hoskins and Wampler (76, 77) who found it impossible to increase the retention of lead arsenate by modification of the electrostatic charges of spray droplets or of sprayed surface.

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PROTECTIVE COLLOIDS AND DISPERSING AGENTS

It is clearly essential that the spray applied shall be of uniform and known concentration, but in the case of certain suspensions

such as lead arsenate or sulphur, this result is not easily attained, owing to the ready sedimentation of the particles. Although there are two obvious ways of reducing rate of sedimentation, namely, using suspensions of finer state of division and agitation by mechanical means, it is often advantageous to use auxiliary spray materials which function either as protective colloids or as dispersing agents.

The precise mechanism by which these materials delay sedimentation is not fully known, but it is probable that the protective colloid is adsorbed at the surface of the particle. The majority of the surface-active materials described above as spreaders are able to act as protective colloids and it is assumed that the particles become surrounded by a shell of adsorbed liquid which, being of similar density to water, delays sedimentation. By Stokes' Law it can be shown that the velocity of fall of the particle surrounded by the liquid shell will vary inversely as the total diameter of the particle and shell. The larger the shell, the slower will be the rate of fall. Further, since the rate of fall is inversely proportional to the viscosity of the liquid medium, substances such as gelatine, dilute solutions of which have a markedly greater viscosity than water, are able to delay sedimentation by virtue of viscosity effects. Woodman (78) examined the efficiency of a number of protective colloids for use with lead arsenate, selecting gelatine as the most suitable.

Dispersing agents produce an effect similar to that of protective colloids, but it is probable that these materials function through their action in dispersing aggregations of amorphous particles. Their action is akin to that of deflocculating agents used, for example, in the treatment of soil suspensions prior to mechanical analysis, in order to break down the soil " crumbs " to prime particle structure. As their action is probably due to adsorption at the particle surface they include the materials described above as spreaders and, in particular, the sulphonated oils, the condensation products of aromatic sulphonates with aldehydes (e.g. dinaphthylmethane disulphonate, 79) and sulphite lye.

Protective colloids and dispersing agents also find an important application in the manufacture of concentrated pastes intended for dilution to spray strength by the grower. Familiar examples are the arsenate of lead pastes, the so-called colloidal sulphurs and the copper pastes. Such products should contain the maximum amount of active constituent, but should not be so viscous that they are

difficult to mix and to measure. If too fluid there is a danger that, on storage, the solid material present will sink to form a tough sediment, difficult or impossible to remix to a uniform paste. By the incorporation of suitable protective colloids and dispersing agents it is possible to prepare pastes of high concentration, yet easily stirred and poured. Examples are the employment of sulphite lye in certain proprietary copper pastes (B.P. 392,556), and of the sulphonated naphthalene-formaldehyde condensation product with salicylanilide (B.P. 350,642).

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EMULSIFYING AGENTS

Oils and other water-immiscible liquids are generally used in a diluted form as spray materials. Such liquids on agitation with water break up to small droplets which, on standing, rapidly coalesce to form a separate layer. This coalescence may be prevented or retarded by the addition of auxiliary materials which, since they stabilize the dispersion or emulsion, are generally called emulsifiers.

With two immiscible liquids such as oil and water, two types of emulsion are possible. Either the oil may be dispersed as fine droplets suspended in water, which is then the continuous phase, giving an oil-in-water (O/W) emulsion, or the water may be the disperse phase giving a water-in-oil (W/O) emulsion. The type of emulsion generally required in spraying practice is the O/W emulsion, which, as water is the continuous phase, is readily diluted with water. The type of emulsion is determined mainly by the nature of the emulsifier present though, as Woodman (80) pointed out, certain emulsifiers may yield either type of emulsion according to conditions.

It is now generally accepted that the principal function of the emulsifier is to modify the properties of the interface between the disperse and continuous phases. In the case of soaps as emulsifiers for O/W emulsions, for example, adsorption of the soap occurs at the interface, the polar group being held by the water, whereas the oil-soluble non-polar group is held by the oil, thus producing a film which resists the tendency of the oil droplets to coalesce. In the same way, every surface-active substance is capable of func-

tioning as an emulsifier, and the majority of the spreaders already mentioned have been suggested and used as emulsifiers. In addition, certain solids such as the freshly prepared Bordeaux precipitate (81) are able to act as emulsifiers. The main requirement, according to Bancroft's explanation of the mode of action of solid emulsifiers, is that the solid should be more easily wetted by one liquid than by the other, that liquid which yields the lower contact angle in contact with the solid being the continuous phase.

The Properties of Emulsions.

The term stability of emulsion has been applied above in connection with the resolution of the emulsion to separate layers of the two liquids. This phenomenon is termed the " breaking " of the emulsion, but there are two other forms of instability of importance in spray practice, namely, the creaming and the inversion of the emulsion.

The *creaming* of the emulsion is due to differences in specific gravity between the dispersed and continuous phases and is named from the analogous creaming of milk. Pickering (81) showed that dilute oil emulsions may be regarded as a mixture of the " cream " and the excess of the continuous phase, for the cream contained 65–82 per cent. by volume of oil. If now undeformable spherical particles of the same size be tightly packed into a given volume they will occupy 74·05 per cent. of that volume. The close agreement of this figure and the oil content of creams led Woodman (82) to consider the cream as the only true emulsion which can exist permanently. It is, however, possible to obtain emulsions containing a greater percentage of the dispersed phase. Pickering prepared emulsions containing as much as 99 per cent. paraffin oil, in which emulsion it would appear that the emulsion droplets are no longer spheres, the tight packing causing distortion of the interfacial films.

If then less than 74 per cent. by volume of oil be present there is a tendency of the emulsion to cream. The rate of creaming will be governed by the difference between the densities of the two phases and by the size of droplet of the dispersed phase. Tar oil-water emulsions cream downwards, for the oil is of density greater than water, whilst the usual type of petroleum emulsion forms a surface cream layer. Creaming must not be permitted in practice, for it would lead to the application of a spray of non-uniform concentration. Woodman (82), who described methods by which creaming can be retarded in the case of petroleum emul-

sions, recommended the addition of cresylic acid to the petroleum oil to lessen the density difference. Except in the case of emulsions of large droplet size the creaming of dilute emulsions may be more easily prevented by efficient agitation in the spray tank.

The *breaking* of an emulsion is the usual method by which the toxic dispersed phase comes into play, breaking occurring immediately after application as in a quick-breaking emulsion or after the evaporation of the greater part of the water which forms the continuous phase. Examples will be quoted later (p. 208) of the relationships between toxicity and speed of breaking, which is, in general, dependent upon the stability of the emulsion. It is clearly imperative that neither the concentrated emulsion employed for the preparation of the spray nor the diluted emulsion in the spray tank should break before application. If, in spite of vigorous agitation, free oil is visible, the emulsion is unsuitable for use as a spray.

The *inversion* of an emulsion is the change in the type of emulsion. An O/W emulsion containing soaps as the emulsifying agent can be induced by the addition, for example, of calcium salts to invert to a W/O emulsion, a change which is shown by the appearance of a thick grease immiscible with water but which can be diluted with oil. An inverted emulsion is useless as a spray, and it implies that the particular emulsifier present must be replaced by one more suitable for the water used for the preparation of the spray. As a general rule, surface-active substances forming water-insoluble calcium or magnesium salts are unsuitable for use as emulsifiers in emulsions to be diluted with hard water, by reason of their tendency to favour inversion.

The Preparation of Emulsions.

There are two general procedures by which emulsions of spray strength can be prepared, firstly, methods of home-preparation more or less foolproof and suitable for recommendation to growers ; sscondly, by the simple dilution of manufactured preparations.

The methods of home-preparation may be classified as follows :

Tank Mixture Methods.—In the early history of the use of oils as insecticides, emulsification was achieved by agitation of the oil with hot soap solutions, e.g. the Riley-Hubbard method for kerosene emulsions and the Yothers boiled soap-oil emulsion. Cold-stirred methods were also used in which the oil was added in small amounts to concentrated cold soap solutions. The soaps,

for reasons already stated, are unsuitable for the preparation of emulsions with abnormally hard or saline waters. In such cases, emulsification was obtained by vigorous agitation of the oil in the spray tank with emulsifiers unaffected by hard water. This method has since been called the " Tank mixture " method, and a wide variety of emulsifiers have been recommended as suitable : e.g. the Bordeaux precipitate (83), sulphite lye (46, 84), blood albumin (63).

Two-solution Methods. Staniland (85) observed that vegetable oils varied in ease of emulsification by shaking with soap solutions, differences which Martin (86) showed were associated with the free fatty acid content of the oil. On this basis he devised a simple method for field emulsification which depends on the high emulsifying powers of soap solutions formed by the addition of free fatty acid to dilute alkali. A suitable liquid fatty acid, e.g. oleic acid, is dissolved in the oil to be emulsified and this solution is added to dilute solutions of alkali, a procedure similar to that proposed earlier by Tutin (87) for the preparation of " Two-solution " tar oil washes. Tutin employed proprietary emulsifiers, but the majority of the oil-soluble acids yielding surface-active salts are suitable for the purpose.

Manufactured preparations which merely require dilution with water to yield the required spray are of two types.

Stock Emulsions. The simpler type of product suitable for dilution by the grower to yield emulsions of spray strength are the stock emulsions which are concentrated emulsions obtained by the processing of oil-water-emulsifier mixtures in an emulsifying mill. The range of emulsifiers available is large, but practical requirements limit the number in actual use. These requirements are, firstly, that the emulsions should be sufficiently stable after dilution with hard water, secondly, that the stock emulsion should be of the highest oil content yet should be of a consistency suitable for easy mixing and measuring. When admixture of other spray materials with the diluted emulsion is required, the emulsifier should be one which does not react chemically or interfere with the biological performance of the added materials. For this reason soaps and other alkali or ammonium derivatives are, on the whole, unsuitable for stock emulsion preparation for which purpose sulphite lye has been recommended (88). Finally, the emulsifier should not accelerate corrosion of the drums in which the stock emulsion is stored.

The main faults of stock emulsions, from the spraying point of

view, are their tendency to cream on storage and the danger that, on exposure to frost, the emulsion may break. This danger may be reduced by the incorporation of anti-freezing materials such as glycerine in the aqueous phase, though some emulsifiers (e.g. sulphite lye) yield stock emulsions which, after freezing, thaw without excessive oil liberation.

Miscible Oils. It would appear that the term " miscible " oil was first applied to certain proprietary petroleum oil preparations introduced in 1904. The expression may be conveniently employed to cover all products which are clear (one-phase) solutions yielding emulsions when diluted with water to spray strength. These include the so-called " soluble " oils employed for lubrication, and the " water-soluble " carbolineums used for wood-preservation, products which were the forerunners of horticultural miscible oils.

They are essentially solutions of an emulsifier in the oil or water-immiscible liquid which ultimately forms the disperse phase of the emulsion.

The emulsifiers present in miscible oils are generally soaps, resinates, sulphonated fatty acids or petroleum beta-sulphonates. To effect satisfactory solution, the addition of a mutual solvent such as cresylic acid and a small content of water is usually required. The majority of miscible oils are therefore, as Woodman (89) pointed out, four component systems, oil-emulsifier-mutual solvent-water. By the critical selection of components it is, however, possible to compound satisfactory miscible oils of high oil content. Care must be taken to ensure that the range of temperatures over which perfect solutions are stable is adequate to prevent danger of layering or separation to two layers of different composition on exposure to frost. The most serious faults of miscible oils, as compared to stock emulsions, are that the range of oils and emulsifiers suitable for miscible oil preparation is limited, and that the emulsifiers are precipitated by too hard or saline water and by certain spray components, thus limiting the range of usefulness of miscible oils. On the other hand, ease of handling and measuring, their high oil content, and, in many cases, the easy visibility of the diluted emulsion when sprayed, are practical advantages which render miscible oils popular with growers.

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CHAPTER VI

FUNGICIDES

The fungi controllable by materials applied as sprays or dusts to the plant may be divided into two main groups : firstly, the ectophytes which, living on the exterior of the plant, may be directly killed by contact with a chemical : secondly, the endophytes which, living within the plant tissue, are assailable by a fungicide only when the hyphæ break through the plant surface to form the reproductive organs. Both ectophytes and endophytes are disseminated by spores which, falling on the plant surface, can be prevented from establishing infection by the action of externally-applied fungicides.

The action of the fungicide on the fungus may thus be : (1) a direct toxic action and (ii) an indirect protective action.

THE SULPHUR GROUP

Sulphur.

The value of sulphur as a fungicide was known prior to the scientific study of the fungi against which it is used. Thus the employment of sulphur, wetted with soap-suds, by Robertson (1) in 1821 has already been mentioned. Its use was greatly extended following the appearance in Europe of the Powdery Mildew (*Uncinula necator* (Schw.) Burr.) of the Vine. This disease, probably introduced from America, rapidly spread in vine-growing districts and caused immense loss until Duchartre, in 1848, recommended the use of sulphur. So effective was the remedy that sulphur has become the most widely used method of control of Powdery Mildews (Erysiphaceæ).

Sulphur is now available from a variety of sources in a number of forms suitable for use either as sprays or dusts. For dust application, " flowers of sulphur," produced by sublimation, was at one time deemed especially suitable on account of its fine state of division. It is now possible, however, to produce ground sulphurs

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of particle size controlled by fractionation by means of a current of air. To this product the name of flowers of sulphur has also been applied, although either the designation " Flour Sulphur " or " Wind-blown Sulphur " would appear happier. The finely-ground sulphurs, probably because of their electrical properties, have an objectionable tendency to " ball," forming small aggregates difficult to disintegrate. This tendency may be overcome by the addition of a small percentage of inert material, such as kaolin, lead arsenate (2), lamp black (U.S.P. 2037090), iodine (U.S.P. 2061185) dicalcium phosphate (U.S.P. 2069568) or zinc oxide (U.S.P. 2069710). In a proprietary dust " Kolodust," finely ground sulphur is mixed with bentonite-sulphur (Kolofog, U.S.P. 1550650), prepared by grinding the products of the fusion of sulphur and bentonite (3).

In addition to these two forms, sublimed and ground sulphurs, there are sulphur-containing by-products which have been used as fungicides. " Green Sulphur " * (Soufre noir) is the spent oxide from a process by which impure coal-gas is passed through hydrated ferric oxide which is afterwards " revivified " in air, when the oxide is re-formed and free sulphur is deposited. A modern development of this process (4), using suspensions of ferric oxide, yields the " flotation " sulphur known as " Ferrox " sulphur. This product, after washing to remove thiosulphate and thiocyanate, may contain 2–6 per cent. ferric oxide. The Thylox liquid purifica-tion process, in which the ferric oxide suspension is replaced by solutions of certain thioarsenites, yields Thylox flotation sulphur. " Gray flotation " sulphur is also produced in the liquid purification of water gas. These three types of flotation sulphur have been widely investigated by American workers (5, 6, 7).

If to be applied as a spray, the finely-divided sulphurs require the addition of a wetter, for the sulphur particles are not wetted by water. Robertson, as has been mentioned, used soap, a practice recommended by Goodwin and Salmon (8), for it permits the application of the sulphur with nicotine washes. " Wettable " sulphurs have been widely introduced in the United States, one of the most popular being " Dry Mix Sulphur-Lime," containing sulphur, casein and hydrated lime, and introduced by Farley (9) as a substitute for lime sulphur (see p. 114). The chief disadvantage of most " wettable " sulphurs is that their rapid sedimentation in

* The term " green sulphur " has also been applied to sulphurs to which a green pigment (e.g. malachite green) has been added to render the deposit on foliage less conspicuous.

the spray tank calls for vigorous agitation to ensure the application of a suspension of uniform sulphur content. By suitable grinding or by precipitation processes it is, however, possible to produce sulphur suspensions of particle size small enough to exhibit Brownian movement and hence termed "colloidal." Certain of the earlier colloidal sulphurs have been examined physically and chemically by Woodman (10). Recent patents for the manufacture of finely-divided or self-dispersible (wettable) sulphurs include B.P. 495393, 499806–7, U.S.P. 2060311.

A third method of applying sulphur is by volatilization. It is probable that the practice of painting the hot-water pipes of vine-houses with sulphur, recommended by Bergmann (11) in 1852, and proved of practical value by Barker, Gimingham and Wiltshire (12) is dependent upon this process. Among the various types of appar-atus which have been proposed for the more efficient volatilization of sulphur, are Campbell's Patent Sulphur Vaporizer, the Rota method due to Rupprecht (13), in which steam is passed over molten sulphur, and Barker and Wallace's (14) method of blowing air over molten sulphur at a temperature below its ignition-point (170°–230° C.).

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Action on the Fungus. The mode of action of sulphur upon fungi has been the subject of much investigation and speculation. The earlier views appear to concern physical properties, for Mangini (15) considered that electricity generated by the contact of plant and sulphur particle was responsible. Mach (16) suggested an optical action the fine sulphur particles forming small lenses which,

focusing the sun's rays on the fungus, kill it by heat. Hence why, in sunlight, sulphured vines appear burnt at those places covered by the fungus !

More recently, attention has been directed to the mechanism of the action of sulphur " at a distance." That fungicidal activity is shown by sulphur applied to a heated surface has led to the suggestion that the toxic agent is a volatile derivative formed in the absence of the host plant. The results of Muth (17), Vogt (18), Goodwin and Martin (19) and Sempio (20) indicated that this volatile agent is non-acidic and discredited earlier suggestions (21, 22) that sulphur dioxide or other oxidation products are responsible for the action of sulphur at a distance. An alternative hypothesis, suggested by Sestini and Mori (23), is that the active agent is sulphur vapour. Barker, Gimingham and Wiltshire (see 24), however, found that the active agent could be removed by filtration through a cellulose pad. In explanation, they suggested that the sulphur moved through space in a finely-divided solid or " particulate " state. As Barker could detect no translocation of the sulphur as a gas or vapour, he considered that the particulate sulphur emanated in the form of minute solid particles from the parent mass. This suggestion was critically examined by Goodwin and Martin (19), who found that provided the filtering medium was at the same temperature as the parent sulphur, the active agent passed the filter. These experiments indicated that it is unnecessary to postulate the existence of any mechanism other than the condensation of sulphur vapour to account for the formation of particulate sulphur and that the volatility of sulphur is sufficient to account for the action of sulphur at a distance. That sulphur exerts a definite vapour pressure at ordinary temperatures was also shown by Tucker (25), who advanced the view that admixture of sulphur with lamp black or other dark-coloured, heat-absorbent substance, would enhance the fungicidal properties of sulphur.

Accepting that sulphur is able to act at a distance by virtue of its volatilization and subsequent condensation to particulate sulphur, the problem is reduced to the mode of action of sulphur in contact with the fungus or leaf.

It was observed by Pollacci (26) and by Selmi (27) that sulphur in contact with living plant tissue gave rise to hydrogen sulphide, an observation extended by Barker (28) who gave lists of fungi and flowering plants able and unable to reduce sulphur in this manner.

McCallan and Wilcoxon (29) found that all the species of plants tested evolved hydrogen sulphide when in contact with sulphur.* It has therefore been suggested that hydrogen sulphide is the cause of the fungicidal action of sulphur. The fungicidal activity of hydrogen sulphide has been established by many observers, including Pollacci. Marsh (32) and McCallan and Wilcoxon found that moist hydrogen sulphide inhibited the germination of the spores of the various fungi examined by an *in vitro*, closed-cell technique. Marsh found no direct correlation between the susceptibilities of the different fungi he examined to sulphur and to hydrogen sulphide, and he concluded that a sulphur-sensitive fungus is one which can act upon sulphur to produce hydrogen sulphide. He suggested the possibility that the toxicity of sulphur to a non-susceptible fungus may be influenced by the character of the host plant. Thus the growth of *Botrytis cinerea* on a sulphur-active plant (i.e. able to reduce sulphur) might be arrested by sulphur, whereas the same fungus on a sulphur-inactive host might be un-affected by sulphur. McCallan and Wilcoxon, on the other hand, found the order of susceptibility to sulphur and to hydrogen sulphide of the eight species of fungus spores examined identical but that, if the production of hydrogen sulphide be expressed in units equal to the amount required to reduce the germination to 50 per cent., the sulphur-sensitive species produced more than one unit, whereas the resistant species produced considerably less than one toxic unit of hydrogen sulphide.

Against actively-growing fungi, hydrogen sulphide has not been proved so effective a fungicide. The observations of Eyre and Salmon (33) that hydrogen sulphide solutions are without effect upon *Sphærotheca humuli* were extended and confirmed by Martin and Salmon (34) who, to secure a greater sulphide sulphur concentration, used sodium sulphide solutions. The fungicidal activity of the alkali sulphide, which decomposes after spraying mainly to hydrogen sulphide and alkali carbonate, was not greater than that of equivalent alkali solutions. Of the simpler sulphur derivatives

* The method of hydrogen sulphide detection employed in these investigations was the blackening of lead acetate paper. Although Barker (24) mentioned the possibility, it has not been definitely disproved that the formation of lead sulphide is due to a volatile organic sulphide. In view of the recent work (see e.g. 30, 31) upon the volatile arsenic derivatives produced by the action of fungi upon arsenical pigments, which have been shown to be alkyl arsenides and not hydrogen arsenide, as was at one time supposed, this possibility deserves re-examination.

examined by these investigators, only sulphur in polysulphide form was found to possess toxicity great enough to account for the fungicidal properties of elementary sulphur. In the presence of excess sulphur or, under certain conditions, of oxygen, hydrogen sulphide reacts to form polysulphide sulphur.

The formation of hydrogen sulphide from sulphur in contact with living tissue was considered by de Rey-Pailhade (35) to be due to a specific enzyme which he named " Philothion." This product has since been identified with glutathione, a tripeptide of glycine, glutamic acid and cysteine, first isolated by Hopkins (36). Barker (24) has suggested that hydrogen sulphide is formed by the action of a reducing agent, probably glutathione, the reaction taking place outside the organism. McCallan and Wilcoxon (29), on the other hand, adduced evidence that the hydrogen sulphide is produced on or within the fungus spore and not on the sulphur. They suggested that the fungicidal activity of sulphur involves the diffusion of sulphur vapour from the sulphur particle to the spore where it is reduced to form hydrogen sulphide. Martin (37) pointed out that hydrogen sulphide is an initial product of the hydrolysis of sulphur, i.e. its interaction with water. The hydrolysis of sulphur in the presence of alkali or lime is the usual method of preparing the polysulphide solutions which are described in pp. 115–116, and the reaction is readily detected under alkaline conditions or under conditions in which one of the products of hydrolysis is removed as, for example, in the presence of copper foil. The formation of hydrogen sulphide from sulphur in the presence of living tissue may therefore be explained by the intervention of the organism to remove a product of hydrolysis.

Under conditions in which the acidity of the products of hydrolysis of sulphur is incompletely neutralized, oxy-acids of sulphur are formed. The suggestion that the fungicidal activity of sulphur is associated with the formation of sulphur dioxide and sulphuric acid (see 21, 38, 39) has already been mentioned. That the toxic derivative is an oxidation product is indicated by the work of Doran (40), Young (22) and Sempio (20), who have shown that oxygen is necessary for the prevention of the germination of various fungus spores by sulphur. Sempio suggested that oxygen made the cell membrane more permeable to sulphur vapour and increased the sensitivity of the spore to toxic agents. If, however, the toxic agent is a product of hydrolysis, oxygen may play the part of an accelerator of the reaction. Young (22), observing that

certain forms of sulphur suspension rich in pentathionic acid, were
more fungicidal than forms containing little pentathionic acid,
considered that this oxidation product was the active fungicide.
His suggestion was critically examined by Roach and Glynne (41)
and by Wilcoxon and McCallan (42) and, in neither study, were
indications obtained that the toxicity of pentathionic acid solutions
is greater than that due to their acidity. Wilcoxon and McCallan
found hydrogen sulphide 6–200 times as toxic as equivalent solu-
tions of pentathionic acid, whilst Roach and Glynne showed that
acidified solutions of sodium thiosulphate, hydrosulphite and for-
maldehyde sulphoxylate about ten times as toxic as pentathionic
acid to *Synchytrium endobioticum*. As this fungus is the soil
organism responsible for Potato Wart Disease its reaction to sulphur
will be considered in more detail under Soil Treatment (p. 290).

Summarizing our present knowledge of the causes of the fungi-
cidal activity of sulphur it may be said that the volatility of sulphur
is sufficient to account for its action across space ; that its activity
in contact with living matter is associated with the formation of
a volatile sulphide, probably hydrogen sulphide ; that hydrogen
sulphide is capable of inhibiting the germination of fungus spores
and, in the presence of excess sulphur and moist air, may give rise
to polysulphide sulphur which is probably responsible for the direct
fungicidal activity of sulphur.

In addition to its inherent toxicity, physical factors, notably
degree of fineness, influence the fungicidal efficiency of sulphur.
It is reasonable to assume that the more finely divided the sulphur
and, hence, the more frequent the points of contact with living
tissue, the greater will be its direct fungicidal properties. Wilcoxon
and McCallan (43) proved that the inhibition of germination by
sulphur dusts of high purity is determined by the number of
sulphur particles. and that the dust which furnishes the greatest
number of particles per unit weight is the most toxic, the relation-
ship being such that if the dusts are compared on the basis of an
equal number of particles per unit area, there is no difference in
toxicity. This rule was not found to apply to impure or " modi-
fied " sulphur dusts.

The adherence of sulphur dusts and sprays to foliage was examined
by Thatcher and Streeter (44), Wilcoxon and McCallan (43),
Hamilton (45) and by White (46), all of whom showed that with
sulphur dusts adherence depends on the degree of fineness.
Hamilton, extending the earlier work of Thatcher and Streeter,

found that there is a rapid initial loss of both spray and dust deposit, due apparently to the removal of excess and coarse sulphur particles, after which the materials tended to rank in tenacity according to the amount of fine sulphur they contained. It may therefore be concluded that particle size plays an important part in determining toxicity and retention and, consequently, the fungicidal efficiency of sulphur dusts and sprays.

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Action on the Plant. It is convenient in describing phytocidal activity to distinguish between acute injury, characterized by the

localized killing of plant tissue (necrosis) and popularly termed
" scorch " or " burn," and chronic injury which involves deep-
seated physiological changes and causes, for example, the stunting
and premature drop of fruit or leaves. This distinction, although
not always clear cut, is permissible because, in many cases, the
two types can be ascribed to unrelated properties of the spray or
dust responsible for the injury.

Acute injury by sulphur is rare in temperate climates but, in
hotter climates, as in Texas (47), severe burning is sometimes
caused by the sulphuring of cantaloupes for the control of Powdery
Mildew (*Erysiphe cichoracearum* DC.) a danger avoided by Milbrath
(48) by placing the sulphur on the soil under the plants. Sulphured
apples grown in semi-arid districts may develop lesions on the sun-
exposed cheek of the fruit, an injury attributed to " sulphur sun
scald."

On the other hand, elementary sulphur is responsible, even in
temperate climates, for the premature defoliation and drop of fruit
of " sulphur-shy " varieties. Among apple varieties, for example,
Stirling Castle and Lane's Prince Albert are particularly susceptible
to sulphur-containing sprays, whilst among gooseberries the use
of any form of sulphur for the control of American Gooseberry
Mildew, *Sphærotheca mors-uvæ* (Schw.) B. & C. on the varieties
Leveller, Early Sulphur and others, results in rapid defoliation.
As this phenomenon has been studied mainly in connection with
the polysulphide sprays, its further discussion is postponed (see
p. 118).

Phytocidal action also arises when sulphur-containing fungicides
are applied during the blossoming period. MacDaniels and Furr
(49) have shown that sulphur dusts on the stigma of apple blossoms
inhibit pollen germination and hence reduce the setting of the
fruit. Hamilton (50) concluded, however, that, as a good fruit
set follows a limited period, at the most two days, of favourable
pollinating conditions, the practice of spraying during bloom for
apple-scab control is commercially feasible.

Instances have been recorded of the beneficial effect of sulphur
on the host plant, apart from the prevention of injury by the fungus.
It has been claimed that, since the introduction of sulphuring into
French vineyards, the average date of picking has been advanced
by about a fortnight. De Castella (51) urged a return to sulphur
in Victoria, not only for the control of Oidium but also on account
of its " tonic " effect on the vine. Fryer (52) stated that the

sulphuring of hops just as the " burr " forms leads to an increased growth of bine, whilst Bobilioff (53) observed an extraordinary stimulus to flowering in over 90 per cent. of the Hevea rubber plantations sulphured for mildew control.

In the case of the impure and by-product sulphurs, phytocidal action may be caused by certain impurities. With the green sulphurs, there is a risk that the presence of tarry matter, and more particularly of thiocyanate compounds, may cause foliage injury.

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Supplements for Sulphur Sprays and Dusts. When sulphur is used as a direct fungicide, the importance of securing good contact with the fungus renders imperative the addition of suitable wetters and penetrants. Goodwin and Salmon (54) drew attention to the more rapid action of wetted sulphur in comparison with dusted sulphur. On the hypothesis that the active fungicide is formed by the hydrolysis of sulphur, Martin (55) suggested that the spreader employed should preferably be alkaline. Spray trials by Goodwin, Martin and Salmon (56) confirmed this conclusion and showed that sulphur applied with soap or lime casein, which are alkaline in reaction, is far more toxic than sulphur applied with gelatine or saponin, which give rise to acid decomposition products. Sempio (57) criticized Martin's interpretation of these results on the grounds that the differences in activity might be associated with differences in the protective colloidal properties of the wetters used. Martin showed, however, that the fungicidal activity of sulphur in gelatine suspension was restored by the addition of non-toxic amounts of alkali. Moreover, Sempio, though obtaining differences in the germination of spores of *Erysiphe graminis* in favour of alkaline sulphur suspensions, was concerned with the activity of sulphur as a protectant. McDaniel (58) also recorded that the addition of lime to a sulphur-bentonite product (Kolofog, see p. 105) increased

the effectiveness of this product for inhibiting the germination of spores of *Venturia inæqualis*. It is, however, reasonable to suppose that the differences in direct toxicity found by Goodwin, Martin and Salmon will not be so marked in protectant value, for the necessary degree of alkalinity will not be long maintained after exposure upon foliage.

In the case of sulphur employed as a protective fungicide, important purposes of the addition of supplementary materials are to render the sulphur particles wettable and to improve tenacity. The superior tenacity of sulphur suspensions over sulphur dusts is shown in the results of Thatcher and Streeter (59), Hamilton (60) and White (61).

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The Polysulphide Group.

Just as oxygen combines with the metallic elements to form oxides, so does sulphur form sulphides. The sulphides of the alkali and the alkaline earth metals are able to combine with further sulphur to form polysulphides. To this group of polysulphides belong a number of commercial products used as fungicides, the three most important being Lime Sulphur, Liver of Sulphur and Ammonium Polysulphide.

Lime Sulphur. Lime sulphur is the product obtained by boiling milk of lime (a suspension of calcium hydroxide) with sulphur and contains in solution a varying amount of calcium polysulphides.

Grison (1), in 1852, suggested a solution, prepared by boiling slaked lime and sulphur in water, allowing the mixture to stand and diluting the supernatant liquid to the requisite strength, as an efficient remedy against Vine Powdery Mildew. This solution, known then as " Eau Grison," is undoubtedly the forerunner of the material later introduced from the United States under the name lime sulphur. It would appear that the fungicidal properties

of lime sulphur were rediscovered in a modification of the sheep-dip known as California wash. This material, prepared by boiling a suspension of lime, sulphur and salt in water, was found to be efficacious against the San José Scale, an insect pest then recently introduced into California. To confer fungicidal properties, Lowe and Parrott (2) added copper sulphate to the mixture but, in one case, recorded some control of Apple Scab (*Venturia inæqualis*) by the lime sulphur-salt mixture. The addition of salt was later found to be unnecessary for insecticidal purposes, and Parrott, Beach and Sirrine (3) found this modified wash very effective in the control of Apple Scab.

As a fungicide lime sulphur rapidly became established and numerous formulæ were proposed for its preparation. Commercial products are now available which have replaced the home-made preparations, the production of which entailed a laborious boiling process. The so-called " self-boiled " lime sulphurs, in which the necessary heat is generated by the slaking of the quicklime, are products which may be more accurately classed as sulphur sus-pensions, for the amount of polysulphide sulphur present is, in most cases, small compared with the free sulphur present which, as it is wetted, can be used as a spray.

The chemistry of lime sulphur is described most easily by con-sidering the reactions occurring when sulphur is heated in lime suspension. The first interaction is one of hydrolysis which may be represented by the summation equation * given below.

In the presence of lime, calcium hydrosulphide and calcium sulphite are formed, the former reacting with excess sulphur to give polysulphide, the latter combining in the alkaline solution with further sulphur to form calcium thiosulphate. The process may therefore be represented by the following equations, in which, for simplicity, the hydrosulphide is represented by the sulphide :

$$3S + 3H_2O \longrightarrow 2H_2S + H_2SO_3$$

$$CaO \Big| S_x \quad CaO \Big| S$$

$$2CaS.S_x \quad CaS_2O_3$$
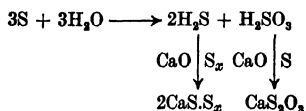
Calcium thiosulphate and calcium polysulphide are therefore the

* Bassett and Durrant (4) regard the initial interaction as

$$2S + 2H_2O = H_2S + S(OH)_2$$
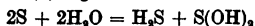
the sulphoxylic acid $S(OH)_2$ reacting in the presence of insufficient alkali to form complex sulphur acids, e.g. thiosulphuric acid (see p. 290).

predominant compounds present in lime sulphur. On storage, oxidation may occur with the formation of calcium sulphate which forms white glistening crystals in the sludge.

The chemical nature of the polysulphides has been the subject of much controversy, the view now generally accepted being that of Pearson and Robinson (5) who showed that the polysulphides exist as such in aqueous solutions and react as if one of the sulphur atoms were unique. The structure of the polysulphides, which is explained by these investigators by the electronic theory of valency, is therefore best represented by the formula $CaS.S_x$, a formula which distinguishes between the sulphur combined in true sulphide form (the " monosulphide " sulphur) and the additional " polysulphide " sulphur. This distinction is of particular importance from the analytical and biological aspects, for it permits a reasonable explanation of the reactions of the polysulphides, and the correlation between chemical and fungicidal properties.

When diluted with water and on exposure to air, lime sulphur undergoes a series of decomposition changes, Firstly, the polysulphides are hydrolysed to a slight extent, giving to diluted lime sulphur an alkaline reaction. As a product of this hydrolysis, hydrogen sulphide is found, a compound which has been shown to play an important part in the reaction of lime sulphur with other spray materials such as lead arsenate (see p. 231). Secondly, on exposure to air, oxidation occurs, resulting in the formation of calcium thiosulphate and free sulphur. Thirdly, lime sulphur is rapidly decomposed by carbon dioxide to form calcium carbonate, hydrogen sulphide and free sulphur :

$$CaS.S_x + CO_2 + H_2O \longrightarrow CaCO_3 + H_2S + S_x.$$
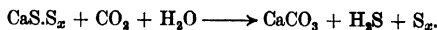
The net result of these three reactions is that when sprayed upon foliage the greater part of the polysulphide sulphur is precipitated as free sulphur, the monosulphide sulphur is dissipated as hydrogen sulphide, the thiosulphate, being water-soluble, will disappear in drainage water from the foliage, and the calcium carbonate, together with any relatively insoluble calcium sulphate which may be present, will remain with the sulphur upon the plant surface.

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Action on the Fungus.   The direct fungicidal activity of the poly-sulphide sprays has been shown by Salmon and his co-workers (6) to depend solely on their polysulphide sulphur content.   Against the Hop Mildew under the biological conditions which Salmon carefully standardized, the amount of polysulphide sulphur necessary to prove fungicidal was equal in every class of polysulphide com-pound and appeared to be independent of the base present.   From their results these investigators deduced that the toxicity of poly-sulphide solutions is due to the polysulphide as such.   Goldsworthy (7) has shown the instantaneous reaction of the spore protoplasm to lime-sulphur solutions and the appearance of elementary sulphur in the germ tube.   He suggested that the oxidation of the poly-sulphide to sulphur is an important factor in the fungicidal action of lime sulphur.

The protective fungicidal action of lime sulphur is due to the elementary sulphur formed by the decomposition of the polysul-phides after spraying.   Because of the rapid action of carbon dioxide on the polysulphides, the amount of sulphur deposited will be determined mainly by this reaction and will therefore be equal to the amount of polysulphide sulphur in the spray applied.   The fungicidal efficiency, both direct and protective, is thus determined by the content of polysulphide sulphur, a criterion which has now been accepted by the Ministry of Agriculture (8) for the evaluation of lime sulphurs as spray materials.

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Effect on Plant.   Lime sulphur damage may be of both acute and chronic types.   The former, described by Young and Walton (9), takes the form of a scorch, browning the tips and edges of the young leaves and forming necrotic patches adjoining the larger veins of older leaves.   When occurring at pre-blossom stages, the check to

leaf growth caused by this injury may seriously aggravate frost-
damage. Wallace (10), in his pioneer work on lime sulphur injury,
concluded that it occurred before the spray had dried on the leaf
and hinted that the soluble forms of sulphur were more caustic
than the dried spray residue. His contemporary Volck (11) similarly
suggested that the soluble sulphides were the prime cause of injury
and recommended the precipitation of the lime sulphur with ferrous
sulphate prior to application. Wallace employed carbon dioxide
for the same purpose and Safro (12) experimented with a number
of metallic salts yielding insoluble sulphides. A similar idea seems
to underlie the " catalytic sulphur " devised by Peterson (U.S.P.
2098257). By such means the monosulphide sulphur is removed
as sulphide and the polysulphide sulphur is precipitated as free
sulphur ; these mixtures may be regarded as wettable sulphurs
rather than polysulphide sprays. As the precipitation of the mono-
sulphide also removes a source of trouble in lime sulphur-arsenate
combined washes, this topic is again discussed on p. 232. Com-
parison of lime sulphur damage with hydrogen sulphide injury
reveals great similarities (13) and the preliminary observations of
Berry (14) support the view that hydrogen sulphide is a factor
responsible for lime sulphur damage.

The phytocidal action of lime sulphur is aggravated by high
temperatures (15) and Howlett and May (16) stated that 26·5° C.
is generally regarded as the danger-point. It is probable also that
weather conditions prior and subsequent to application affect the
response of the plant by their influence on the physiological condi-
tion of the foliage. Thus McCallan, Hartzell and Wilcoxon (13)
found, in some cases, that wilted plants withstood hydrogen sul-
phide better than turgid plants. Similarly the nutritional status
of the plant influences phytocidal response which, in the case of
lime sulphur injury, is generally more apparent upon apple trees
deficient in nitrogen. Wallace (17) cited evidence of the greater
susceptibility to sulphur sprays of trees suffering magnesium
deficiency as judged by the examination of the leaf ash constituents.

Chronic lime sulphur damage has a peculiar characteristic in that
the spray causes a premature abscission of leaves and fruit without
necessarily causing marked leaf scorch. This phenomenon, already
mentioned under sulphur (see p. 112), was originally considered
specific in polysulphide sprays, but Martin (18) found defoliation
of sulphur-shy gooseberries was not prevented by the precipitation
of lime sulphur by aluminium sulphate prior to application, in which

case, elementary sulphur is the responsible agent. The drop of young fruit when lime sulphur is used against Apple Scab may prove serious. According to Sanders (19) the substitution of Bordeaux mixture for lime sulphur in the Annapolis valley apple-growing district of Nova Scotia resulted in a doubled output.

The reasons for abscission and sulphur sensitivity are obscure, but the process was shown by Volck (11) to be analogous to that causing normal leaf-fall. An entry of the responsible constituent into the leaf seems necessary and Sanders (20) concluded that this is effected at the stomata, for when he sprayed lime sulphur only upon the fruit and upper apple-leaf surfaces, which bear no stomata, fruit-drop did not occur. He suggested, on finding a degradation of the chlorophyll of the palisade cells, that the fruit and leaves are starved off by the reduction in photosynthetic activity, a reduction of more serious consequences in regions or seasons of low sunlight. Berry (14) questioned the application of this hypothesis in cases where the shed leaves show no visible injury and suggested that penetration of hydrogen sulphide is the first part of the process, the hydrogen sulphide accelerating enzyme activity and causing premature defoliation. One merit of this hypothesis is that it brings into line lime sulphur and sulphur damage, for hydrogen sulphide is a product of the decomposition of the former material and is a product of biological activity in the case of sulphur.

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Supplements for Lime Sulphur. When lime sulphur is employed as a direct fungicide, the addition of a spreader is essential to secure full efficiency. Soaps and other spreaders yielding insoluble calcium salts are useless and, until recent years, lime casein (21) was widely used. Gelatin and saponin have also been recommended,

and Goodwin, Martin and Salmon (22) showed that the polysulphides differ from elementary sulphur in that the acid or alkaline character of the spreader has but little effect upon fungicidal activity.

When used as a protective fungicide, lime sulphur has generally been applied without a spreader, a suitable spray deposit being obtained by the avoidance of excessive spraying. The addition of lime casein was at one time frequently suggested, particularly in America, but Goodwin and Martin (23) gave evidence that the addition of lime casein containing a large excess of free lime may cause a reduction in the amount of sulphur deposited owing to the formation of an increased amount of calcium thiosulphate. On the other hand, in the presence of a spreader, the sulphur is deposited in an amorphous form likely to be more tenacious than the crystalline form otherwise deposited.

An older method of increasing the adherence of the lime sulphur deposit was by the addition of a soluble copper or iron salt. The use of copper sulphate in the California wash (lime sulphur-salt) and the recommendation of ferrous sulphate as a corrective for lime sulphur spray damage have already been mentioned. In both cases the gelatinous precipitate produced is remarkably tenacious and, being clearly visible when applied to foliage, the wash is easier to apply correctly than lime sulphur alone. Dutton (24) remarked that the addition of ferrous sulphate to lime sulphur to serve as a " marker " has been practised to a considerable extent in certain apple-growing districts of the United States.

The use of oil emulsions with lime sulphur sprays was tried by Talbert (25) who reported favourably, but commented upon injury resulting from application at the calyx stage. The majority of the American recommendations now advise caution in the use of hydrocarbon oil sprays for a period within two or three weeks of the application of sulphur sprays. The precise reasons for the injury reported are not apparent and, in this country, trials carried out at Long Ashton (26) of oil-lime sulphur sprays have not given this damage. Nevertheless, care should be taken in recommending the addition of either oil emulsions or ferrous sulphate to lime sulphur for full evidence of the ultimate effect of these combinations on the plant is not yet available.

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Dry Lime Sulphur.

An important disadvantage of lime sulphur is that it is a liquid containing a large proportion of water. The cost of containers and transportation is therefore high. Of the attempts to introduce satisfactory solid substitutes, one of the most successful has been Dry Lime Sulphur introduced in America about 1918. This product is patent-protected (U.S.P. 1254908) and is made by the evaporation of liquid lime sulphur in the presence of a stabilizer (e.g. sugar) to prevent excessive decomposition of the polysulphides. The final product is guaranteed to contain 70 per cent. calcium polysulphides and 5 per cent. sulphur. Hamilton (27) concluded that the product was the best of the lime sulphur substitutes that he tested.

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Liver of Sulphur. Liver of sulphur is the product obtained by the fusion of an alkali carbonate with sulphur. The name is derived from the peculiar liver-like colour of the freshly-exposed surface and dates from a time prior to the distinguishing of the two alkalis, soda and potash. As the alkali then most readily available, and therefore generally used, was the crude potassium carbonate, the term liver of sulphur came to be applied solely to the potash form. Both potash and soda livers of sulphur, as solids or in solution, are now on the market and have found use as fungicides.

The compounds present are analogous to those of the lime sulphur solution, the predominant constituent being the polysulphide of the alkali employed. The proportion of alkali thiosulphate is variable and is dependent not only on the mode of preparation of the liver of sulphur but also upon the time and conditions of storage. In addition, the proportion of sulphate present is greater in liver of sulphur than in lime sulphur, for whereas calcium sulphate is relatively insoluble and remains in the sludge of the lime sulphur, the whole of the alkali sulphate formed will go into solution with the liver of sulphur.

Effect on the Fungus. The activity of the alkali polysulphides of the liver of sulphur solution is, as with lime sulphur, entirely dependent upon the polysulphide content. The alkali present, whether potash or soda, appears to play no part and, although Foreman (28) stated that the use of soda increased the fungicidal value of livers of sulphur, Goodwin, Martin and Salmon (29) found no such increased efficiency with sodium polysulphides against the Hop Powdery Mildew.

Effect on the Plant. The occasional injurious action of lime sulphur is also shown by liver of sulphur solutions and, although there are fewer reports of spray injury by liver of sulphur (which has never found the wide application of lime sulphur), the general view appears to be that there is a greater liability of damage. Possibly this is because the liver of sulphur solutions are more caustic than lime sulphur solutions, for the hydroxides and carbonates both of potassium and sodium are much more strongly alkaline than those of calcium.

Supplements. The spreaders which find use with lime sulphur may be used equally well with liver of sulphur, and the same precautions regarding the type of lime caseins to be employed hold. Liver of sulphur has, however, the additional advantage that soap may be added, for no objectionable calcium curd will now be formed.

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Ammonium Polysulphide. This material—the well-known Yellow Ammonium Sulphide of the analytical laboratory—was recommended first in 1916 by Eyre and Salmon (30). Because of the disfiguring deposit on the gooseberry when lime sulphur is employed against the American Gooseberry Mildew, *Sphœrotheca mors-uvœ*, these workers sought for a spray material by which this objection could be overcome. Liver of sulphur, which would leave a deposit of alkali carbonate and sulphate easily washed off by rain, was tried, but it proved inefficient. It may be observed that, at the time of these experiments, analytical methods for the determination of the polysulphide content were not available and no check on the material used could be made. At a strength which proved fungicidal the liver of sulphur solutions caused severe injury and were therefore discarded. Ammonium polysulphide, which

likewise leaves no objectionable deposit on the fruit, proved so successful that Eyre and Salmon not only recommended this material as a fungicide, but advanced complete methods for its manufacture. There thus arose the " A.P.S., 1918," (31) and the " A.P.S., 1919 " (32). The ammonium polysulphide solutions (A.P.S.), so prepared, are deep-red liquids with a most objectionable odour. Like the other polysulphide sprays they undergo decomposition on exposure.

The chemistry of the ammonium polysulphides is analogous to that of lime sulphur, the solution containing as the active ingredient ammonium polysulphide. The amounts of ammonium thiosulphate and ammonium sulphate present are usually slight owing to the absence of oxygen during the preparation, but tend to increase on storage. On oxidation, the polysulphide sulphur is thrown down as free sulphur, but the reactions here are not quite analogous to those of the calcium, sodium or potassium polysulphides, owing to the volatility of the base present. Thus, if a solution of ammonium sulphide containing no polysulphide sulphur is exposed to air, the yellow colour characteristic of polysulphide sulphur appears. The exact process of the oxidation is unknown, but it appears likely that with the ammonium polysulphides a greater proportion of the sulphur present in sulphide form will be deposited as free sulphur than with the other polysulphide compounds.

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Calcium Monosulphide. In 1929 Hurt and Schneiderhan (33) reported the successful use of calcium sulphide U.S.P. as a protective fungicide against *Venturia inæqualis*. This product, prepared by the reduction of calcium sulphate, contained 60–65 per cent. calcium monosulphide, anhydrous calcium sulphate and a small proportion of powdered coal. A similar product was later introduced as a spray material under the name Cal-Mo-Sul.

Martin and Salmon (34) found calcium monosulphide without direct fungicidal properties to *Sphærotheca humuli* and the general conclusion of American work in the field is that the product is a mild fungicide, the chief advantage of which is the absence of phytocidal properties. Hamilton (35), for example, found Cal-Mo-

Sul less effective than other sulphur sprays in the control of severe scab infestation.

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THE COPPER GROUP

The largest and most important group of fungicides in present use contain as their active agent some form of copper, and of this group the first and still the most valuable is the material known as Bordeaux mixture. The other members of the group which find practical employment are modifications of this mixture and will be treated in historical order rather than order of importance. Recent developments of knowledge of the mode of action of copper fungicides have resulted in the introduction of a number of materials which, not being basic copper derivatives, cannot be regarded as modifications of Bordeaux mixture. A description of the general properties of these compounds will precede a discussion of the action of the copper fungicides on fungus and leaf plant. As the rational choice of supplements is dependent on knowledge of the mode of action of the active constituents, this subject will be treated last.

Bordeaux Mixture.

In 1882, Millardet, investigating the Downy Mildew of the Vine (*Plasmopara viticola* Berl. and de Toni), a disease then recently introduced from America, observed that along the roadside at Medoc in the Gironde, certain vines bore leaves though elsewhere they had been defoliated by the disease. Attributing this persistence of the foliage to some treatment, he found on inquiry that it was the practice to daub the leaves of these particular vines with verdigris or with a mixture of lime and copper sulphate. For this reason, passers-by, thinking the fruit below would be similarly treated, would not touch it for fear of poison. Millardet followed up this slender clue and, in 1885, was able to announce the successful use of a lime-copper sulphate mixture as a fungicide against Plasmopara (1).

The value of the new fungicide, called Bordeaux mixture from the locality in which it originated, was rapidly established and

improvements in the original formula followed at once. Millardet had proposed the admixture of 5·71 parts of copper sulphate and 10·71 parts of quicklime to 100 parts of water, giving a thick slushy liquid which had to be applied with a brush made of twigs. With the help of a brass-worker named Vermorel, he improved the spraying apparatus then available—the Riley or Barnard nozzle —by introducing the degorger, but spraying with his mixture was still difficult. By 1887 Millardet and Gayon (2) recommended the proportion 3 parts of copper sulphate and 1 part of calcium oxide to 100 parts of water, a 3 per cent. spray, and suggested the use of a similar ratio for a 2 per cent. and even a 1 per cent. spray. These formulæ were adopted and are still in use in France. Gradually, with established practice, the formula of the Bordeaux mixture favoured for a particular locality and for a particular crop became fixed, not so much on a scientific basis but because of its continued success. That such an empirical selection unconsciously led to a rational choice may be observed after a more detailed study of the chemistry of the mixture.

The chemistry of Bordeaux mixture is complex and has provoked much research. The form of copper sulphate which is the starting-point of Bordeaux mixture preparations (" bluestone " or " blue vitriol "), is the pentahydrate $CuSO_4.5H_2O$. Its aqueous solution has a slightly acid reaction, generally attributed to small amounts of sulphuric acid formed by hydrolysis. * When lime (calcium hydroxide) is added it combines with the free acid forming calcium sulphate and water. Further copper sulphate undergoes hydrolysis and the acid is neutralized by the lime until all the copper sulphate is decomposed. Millardet and Gayon thought that this decomposition proceeded according to the equation :

$$CuSO_4 + Ca(OH)_2 = Cu(OH)_2 + CaSO_4$$
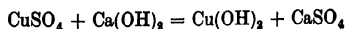
As late as 1907 Bell and Taber (3) claimed that the precipitate of Bordeaux mixture would consist of the three solids, lime, gypsum (calcium sulphate) and cupric hydroxide. Millardet and Gayon observed, however, that neutralization of the acidity is completed not at the equimolecular rate required by the above equation, but before this amount of lime has been added. Pickering (4),

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* One interesting suggestion is that the acidity is due to the formation of a mono-hydrated copper sulphate of the structure, $HO.Cu.O.SO_2.OH$, a constitution which serves as the basis of many basic copper salts, e.g., the trioxysulphate may be represented as $HO.Cu.O.Cu.O.SO_2.O.Cu.OH$ and the basic carbonate as $HO.Cu.O.CO.O.Cu.OH$.

Sicard (5), Wöber (6) and Martin (7) showed that neutrality and complete precipitation of the copper are reached when 0·75 equivalent of lime has been added. The initial product of the precipitation of copper sulphate by calcium hydroxide at ordinary temperatures is therefore the trioxysulphate $4CuO.SO_3.3H_2O$. The precise degree of hydration of this compound is unknown, but the formula cited is that derived from the phase rule studies of Posnjak and Tunell (8) at 50° C.

In the commonly-used Bordeaux mixtures, the amount of lime employed is greatly in excess of that required to precipitate the total copper present and further interaction between the trioxysulphate and the excess lime is shown by the slow disappearance of alkalinity. Pickering (4) ascribed this change to the production of sulphates more basic than the $4CuO.SO_3$ compound, but his conclusions were disputed by Sicard (5) and by Wöber (6), who advanced divergent suggestions concerning the nature of these more basic sulphates. These three investigators agree that the reactions involve the preliminary precipitation of the copper as trioxysulphate, that the interaction of this compound with excess of lime forms compounds of a more basic character and that there is an intermediate stage between the complete precipitation of the copper and the appearance of permanent alkalinity. Martin (7) returned to the older view that the precipitate of freshly-prepared Bordeaux mixtures is cupric hydroxide. His conclusion is based on the observation, by electrometric methods, that permanent alkalinity is not reached until an equimolecular quantity of lime has been added and upon the analogous cupric chloride-lime interaction. Cupric hydroxide is a blue gelatinous precipitate which, when prepared from the chloride, undergoes a peculiar dehydration resulting in the formation of black cupric oxide. Martin suggested that the blue precipitate of Bordeaux mixture is stabilized by adsorbed calcium sulphate and showed that if the moist or dried precipitate is washed with carbon-dioxide-free water, it undergoes dehydration. When applied to foliage, however, no tendency is shown by the Bordeaux deposit to blacken, and Martin indicated that the cupric hydroxide-calcium sulphate complex undergoes an *in situ* change, associated with atmospheric carbon dioxide, to a compound not converted to cupric oxide on continued leaching with water.

The weathering of Bordeaux mixture was studied by Wilcoxon and McCallan (9), who support the view that the precipitate is an

adsorption complex (or solid solution). They found a continual increase in the copper content of the precipitate when exposed as a spray deposit, a change in composition accompanied by an increase in the copper dissolved by the leaching water and not displayed in the washing of Bordeaux precipitate in bulk. The part played by atmospheric carbon dioxide in the weathering process must receive further attention (see p. 138) in connection with the action of Bordeaux mixture on the fungus.

The hydroxide-sulphate complex if allowed to stand with excess lime ultimately forms a violet-coloured precipitate which is probably a calcium cuprite of the type CuO.3CaO postulated by Pickering (4) and Sicard (5). For reasons given in the following section it is necessary to use freshly-prepared Bordeaux mixtures and, as the excess lime is rapidly converted to carbonate when exposed to air, it is probable that calcium cuprites do not enter into the chemistry of Bordeaux mixtures.

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The Preparation of Bordeaux Mixtures. In the actual preparation of Bordeaux mixture, it is usual to add the copper sulphate to the diluted lime, the reverse of the process considered above. The ultimate products of the reaction have been shown by Pickering and by Wöber to be identical whatever the method of mixing. Pickering found, however, that the physical state of the precipitate is influenced by the method of preparation. For spraying purposes, it is necessary that the precipitate should be as finely divided as possible. He found the most suitable precipitate is obtained when the copper sulphate is added, in as concentrated a solution as possible, to the lime suspended in the bulk of the water. Other workers are less drastic in their directions for the preparation of a satisfactory Bordeaux mixture. Butler (10) obtained an unsatisfactory precipitation only when concentrated solutions (stock

solutions) were mixed direct without previous dilution. All are agreed, however, that above normal room temperatures the physical nature of the precipitate is inferior.

Because of the intermediate stage of temporary alkalinity there arise two types of Bordeaux mixture, the neutral and the alkaline. In some cases an acid Bordeaux mixture has been described, but strictly speaking this mixture belongs to the neutral type. Neutral Bordeaux mixtures are prepared so that the lime present is in excess of that required to neutralize the copper sulphate but insufficient to bring about permanent alkalinity. For neutral Bordeaux mixtures the ratio of bluestone to quicklime would be approximately 1 : 0·3, whereas with alkaline Bordeaux mixtures the ratio would be not less than 1 : 0·5.

Of the neutral Bordeaux mixtures, the commonest is the " Woburn " formula advanced by Pickering, which he considered more efficient than the old " normal " 1·6 spray (see below). This he prepared by the addition of clear lime water (a solution of calcium hydroxide) to the copper sulphate solution until no further copper remains in solution to give a coloration with a solution of potassium ferrocyanide. A similar preparation was proposed and used in Italy by Cavazza (see 10) in 1886. The 1887 formula of Millardet and Gayon to which reference has already been made also belongs to the neutral type.

The more common basis for the preparation of Bordeaux mixture is the use of equal weights of bluestone and quicklime. By such means distinctly alkaline Bordeaux mixtures are produced. A convenient method of writing the formulæ is in the form of a ratio giving the weight of bluestone, the weight of quicklime and the volume of water to be used. In this way a 1 per cent. Bordeaux mixture prepared from equal weights of the two ingredients would be written 10 : 10 : 100, the 100 representing 100 gallons (i.e., 1000 lb.) of water. The Bordeaux mixture recommended by Salmon (11) as a potato spray in England would then read 14 : 9 : 100, an alkaline Bordeaux of a less basic character, whereas the older so-called " normal " 1·6 spray would be represented by 16 : 16 : 100.

The actual strength of the Bordeaux mixture most suitable for use is governed by the type and age of the foliage sprayed. No general prescription can therefore be given, but in general it may be said that for the younger foliage a weaker Bordeaux mixture is required to avoid spray injury. It has also been claimed that the more alkaline Bordeaux mixtures are less liable to cause damage

to the foliage, but this is a point which must be reserved for the discussion of the effect of Bordeaux mixture on the plant.

The preparation of Bordeaux mixture under practical conditions is undoubtedly troublesome and various proposals have been made to obviate some of the difficulties. Ricaud (12) suggested the use of a stock solution of the copper sulphate usually prepared at the rate of one pound of bluestone per gallon, a solution which will keep indefinitely. It is often difficult to secure a satisfactory supply of quicklime, hence the use of " hydrated lime," a commercial form of calcium hydroxide, has been recommended by Goodwin and Salmon (13). The employment of a good grade of hydrated lime in place of quicklime was also found satisfactory by Holland, Dunbar and Gilligan (14), who, however, suggested that to secure a better precipitate, the suspension of the hydrated lime should be allowed to stand a while before the addition of the copper sulphate solution. Care must be taken with the storage of both quicklime and hydrated lime, for both rapidly carbonate on exposure to air. If hydrated lime be used allowance must be made for its smaller content of calcium oxide and the 1 per cent. Bordeaux mixture becomes 10 : 15 : 100, the weight of hydrated lime being half as much again as that of quicklime. In America it has become the practice to add granulated (" snow ") bluestone direct to water in the spray tank, solution being obtained by vigorous agitation. The required amount of hydrated lime is then washed into the tank through a sieve, a procedure said to give a satisfactory spray which has been called " Instant Bordeaux " (15).

To obviate the trouble and time involved in the preparation of Bordeaux mixtures, attempts have been made to utilize already-prepared Bordeaux precipitates. The dried precipitate of ordinary Bordeaux mixture is a far from satisfactory material, but Pickering (16) has been able to show that the precipitate of neutral Bordeaux mixture may be so employed. The trioxysulphate is too dense in character to remix satisfactorily, but the more basic precipitates reproduce a mixture which well duplicates the original Bordeaux mixture. " Bordorite," a Bordeaux paste prepared in this manner, has found favour among English fruit and potato growers.

Finally, a serious disadvantage of Bordeaux mixture is that it must be used immediately after preparation. The gelatinous and adherent precipitate of the freshly-prepared Bordeaux mixture undergoes profound physical changes on standing ; that of the

P.P.   K

neutral Bordeaux mixtures becomes granular, whilst that of the alkaline Bordeaux mixtures becomes definitely crystalline in character. The calcium sulphate present passes to long needle-like crystals, whilst the copper compounds form characteristic spherical crystalline bodies. In this way the physical properties of the mixture as a spray rapidly deteriorate.

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Burgundy Mixture.

In 1887 Masson (17), finding difficulty in procuring a suitable supply of quicklime for the preparation of Bordeaux mixture, proposed its substitution by soda (sodium carbonate). This substitute has since received the name of Burgundy mixture, from the district in which it was first employed. A similar mixture was recommended for use in Ireland for potato spraying (18) under the name Soda Bordeaux.

The main chemical reaction taking place when copper sulphate and sodium carbonate solutions are mixed is one of neutralization, the sodium carbonate reacting with the free acid which results from the hydrolysis of the copper sulphate. Carbon dioxide is therefore evolved and produces secondary reactions. Pickering (19), studying the relative amount of sodium carbonate required to secure (almost) complete precipitation of the copper and also permanent alkalinity, found that these points occur simultaneously when 1·6 molecules of sodium carbonate are added to 1 molecule of copper sulphate. Because of the coincidence of these two points, a feature not shown by the lime-copper sulphate mixture, Pickering concluded that with the soda-copper sulphate mixture the reaction is simple, resulting in the formation of the $10CuO.4CO_2$ basic carbonate and sodium sulphate, while the carbon dioxide evolved is combined with the sodium carbonate to form the bicarbonate. Mond and Heberlein (20) concluded that neutrality is reached at the molar ratio of 1 : 1. Actually neutrality was attained by the

addition of an amount of soda less than the theoretical because part of the copper is precipitated by the hydrolysis. Such a mixture contains, however, a considerable amount of copper in solution, due, as these workers show, to the presence of carbon dioxide. When the carbon dioxide was removed by a current of air no trace of soluble copper could be detected. Further addition of soda immediately led to permanent alkalinity, confirming Pickering's observation that there is no stage of temporary alkalinity. The ratio proposed by Pickering as representing the point of neutralization was shown by these workers to be the point of minimum amount of soluble copper, due evidently to the removal of the carbon dioxide by the excess sodium carbonate, the copper in solution thereby being precipitated. If larger amounts of sodium carbonate than the molar ratio of 1·84 to 1 are added, more copper goes into solution by the formation of complex compounds containing electronegative copper.

According to Pickering, the precipitate obtained with the 1 : 1·84 mixture is the basic carbonate $5CuO.2CO_2$, a bulky blue precipitate which gradually changes on standing in the mixed liquid to malachite, $2CuO.CO_2$, a dense green precipitate unsuitable as a spray material. Mond and Heberlein considered that the precipitate obtained at 15° C. with the 4 : 4·25 mixture contained various basic copper sulphates and a basic copper carbonate. They were of the opinion that no well-defined compound of copper appears but that the composition of the precipitate varies according to the conditions of precipitation. The precipitate undergoes the change from colloidal to crystalline, the change being retarded by the presence of free sodium carbonate. For this reason the precipitates of Burgundy mixtures prepared with sodium carbonate in excess of the ratio 1 : 1·84 retain longer their flocculent nature.

Pickering recommended the ratio 1 : 1¾ (accurately 1 : 1·84) as the most suitable for the preparation of Soda Bordeaux. Mond and Heberlein, on the other hand, concluded that the ratio 4 : 4·25 would give the Burgundy mixture possessing the highest fungicidal efficiency. Formulæ used in practice vary, but are generally of 1 per cent. crystalline copper sulphate with a soda content of between 1 and 1·4 per cent., i.e., 10 : 10 : 100 to 10 : 14 : 100, those with the smaller ratio of soda containing free copper sulphate, usually accepted as insufficient in amount to cause serious spray injury.

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The Cuprammonium Group.

When excess of ammonium hydroxide is added to a solution of a copper salt the ammonia combines with the copper to form a cuprammonium salt. Copper sulphate in solution undergoes two types of decomposition : firstly, electrolytic dissociation resulting in the formation of free electropositive copper ions and an equivalent number of free electronegative sulphate ions ; secondly, hydrolytic dissociation resulting in the formation of traces of a basic copper compound and of free sulphuric acid. If now ammonium hydroxide be added, neutralization of the sulphuric acid takes place and a basic copper compound is thrown down which, with excess of ammonia, is redissolved to form the deep blue solution of cuprammonium sulphate. This salt is subject to electrolytic dissociation forming electro-positive cuprammonium ions and a corresponding amount of electro-negative sulphate ions.

The exact nature of the cuprammonium ion is not known and there appear to exist cuprammonium compounds with various proportions of ammonia in conjunction with the copper. In the case of the cuprammonium sulphate the cuprammonium ion may be represented by the formula $Cu(NH_3)_4$ (see, however, 21). The cuprammonium salts are not subject to the hydrolytic dissociation by which free sulphuric acid is formed. The two factors to which the spray injury characteristic of solutions of copper salts are ascribed, namely, free soluble copper and free sulphuric acid, are therefore absent in the cuprammonium sulphate. As, however, the cuprammonium sulphate is decomposed after spraying to form basic copper compounds, it is evident that the cuprammonium sulphate will possess fungicidal properties.

The deep blue solution obtained by the addition of excess of ammonium hydroxide to solutions of copper sulphate was first proposed as a spray by Audoynaud (22) in 1885. The solution had previously received the name of " **Eau Céleste**," presumably from its colour, the blue of the sky ; it has since been called " Azurin." The solution is unstable and requires the presence of a large excess of ammonia to prevent the formation of a precipitate. For this reason various proportions of copper sulphate and am-

moniumhydroxide have been proposed, and it is impossible to give a standard formula for its preparation.

Audoynaud had proposed the use of this material for spraying late in the season, for it does not leave the objectionable deposit upon the fruit which results with Bordeaux mixture. Further, it is more easy to spray and the wear of the sprayer nozzle is less severe because of the absence of solid particles. Unfortunately the material often caused severe foliage injury, which was attributed to the ammonium sulphate in solution, a known cause of leaf "scorch."

To obviate this scorching Patrigeon (23) proposed the use of a solution of precipitate of Burgundy mixture in excess of ammonium hydroxide. The original formula was to prepare a 10 : 15 : 100 Burgundy mixture and to dissolve the precipitate by the addition of a suitable amount of ammonia. This wash was at one time widely used in the United States under the name of " **Modified** " **Eau Céleste.**

To simplify the manufacture of Patrigeon's modified Eau Céleste, Gastine (24) proposed the direct solution of basic copper carbonate in ammonium hydroxide. A closely-related product, obtained by the solution of copper carbonate in ammonium carbonate solution, was suggested by Chester (25). The basic copper carbonate of commerce is usually identical in composition with the mineral malachite, $Cu(OH)_2.CuCO_3$. This material dissolves in ammonium hydroxide in the presence of ammonium carbonate to give a cuprammonium carbonate. According to Ephraim (26), the cuprammonium carbonate stable at ordinary temperatures contains the copper in association with two ammonia groups giving the ion $Cu(NH_3)_2$.

Solutions of basic copper carbonate in ammonium hydroxide or carbonate were at one time popular in the United States under the name " **Cupram.** " They were used mainly as direct fungicides but, with fuller realization of the importance of applying protective fungicides before the attack on the host plant has developed, they have fallen out of use.

Ammonium carbonate may also be used in place of the hydroxide with copper sulphate. A mixture of copper sulphate and ammonium carbonate, ground ready for solution, was suggested by Johnson (27) in 1890. Johnson's mixture is the forerunner of Cheshunt Compound (28), a mixture of 2 parts by weight bluestone and 11 parts ammonium carbonate, recommended for the control of

" damping-off " diseases. The chemistry of these mixtures is complicated, for the hard vitreous ammonium carbonate of commerce is a mixture of the bicarbonate, NH_4HCO_3 and the carbamate $(NH_4)CO_2(NH_2)$. On exposure to air, the decomposition of the latter compound to form the bicarbonate enables the material to be easily powdered.

The cuprammonium solutions, after spraying, all decompose to form residues of basic-copper compounds of properties akin to those of the Bordeaux and Burgundy precipitates.

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Miscellaneous Basic Copper Sprays.

Of the remaining basic copper derivatives, the majority appear as the active constituents of proprietary products. As the field performance of such compounded materials is affected by factors other than the nature of the active ingredient, specification of this latter may not necessarily indicate the efficiency of the product. Nor is it safe to apply the results of trials of a particular product compounded from, for example, basic copper chloride, to all products based on this compound. Further the object of compounding and the justification for the use of the proprietary names is to enable the simple foolproof preparation of a copper fungicide whereby the difficulties of the home manufacture of Bordeaux mixture and its heavy wear on spray machinery may be avoided. The extent to which the manufacturer claims these advantages in compounding his product is not indicated by the statement of nature and content of active constituent.

Of uncompounded basic copper derivatives, the acetate or **verdigris** has been long used in France where it is made by the action of the acid " marc " or residue of grapes on sheet copper. Verdigris consists mainly of basic cupric acetates, the composition of which is determined by conditions during manufacture. It should not be confused with the patina of basic sulphate, carbonate or chloride on copper exposed to atmospheric corrosion. Although

the particular verdigris preparations ("Vert de Montpelier" and "Verdet gris extra sec") used appear to be good fungicides they are probably too expensive for extensive use. Butler and Smith, (29), however, recommended the basic acetates especially where a colourless spray deposit is required.

Recently trials have been made of the basic arsenates, in particular that represented by the formula $Cu(CuOHAsO_4)$, primarily as insecticides (30). The promising fungicidal properties of so stable and insoluble a basic copper derivative are of interest in connection with the mode of action of the copper fungicides.

Of compounded products containing basic copper derivatives, the majority so far introduced have been pastes. Bordorite, based on Pickering's work (31), has been mentioned (p. 129) but has been largely supplanted by Bouisol (B.P. 392556). These products are made from copper sulphate, but a cheaper raw material is the basic chloride $CuCl_2.3Cu(OH)_2$. This compound, frequently called the oxychloride, is analogous in comparison to the precipitate of neutral Bordeaux mixture $4CuO.SO_3$, and is readily formed by the action of air on cupric chloride solutions or scrap copper. It is the active constituent of "Kupferpaster Bosna" (32) and "Caffaro" (33), at one time popular on the Continent. Cuprenox (B.P. 452950), a recent representative of this group, is of interest in that sedimentation to a putty-like deposit, a frequent disadvantage of the older pastes, is overcome by admixture with sulphite lye to a suspension showing marked thixotropy. On standing, the suspension becomes extremely viscous and non-sedimenting but, on agitation, it becomes free-flowing. Unfortunately corrosive action necessitates the use of expensive glass or wooden containers for which reason powders of the self-dispersing types which can be packed in waxed paper packages are more economical. A variety of powders compounded, usually, from the basic chloride are on the European market (34).

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Normal Copper Derivatives.

It had been observed that the addition to Bordeaux mixture of supplements containing reducing sugars, e.g. sulphite lye or molasses (35) led to a slow reduction of the basic precipitate to yellow cuprous oxide. Contrary to Holland, Dunbar and Gilligan's suggestion (36) Martin (37) found that this change was not accompanied by a reduction of fungicidal efficiency. It therefore appeared that cuprous oxide was itself fungicidal and a survey (38) revealed that a wide range of relatively insoluble cuprous and cupric derivatives shared protective fungicidal properties. Contemporary work in the United States also revealed innumerable possibilities in devising copper fungicides outside the range of basic derivatives tried by earlier workers. Many of these investigations were based upon hypotheses concerning the nature of the fungicidal action of copper, but it is here proposed to deal only with the chemical and historical aspects.

Cuprous oxide was found by Horsfall (39) an effective fungicide for the control of " damping-off " of vegetable seedlings and was subsequently used as a spray material (40). Cuprous cyanide, which had previously been found to possess insecticidal properties (see p. 171) was shown to be fungicidal by Marsh *et al* (38).

Of cupric derivatives the phosphate $Cu_3(PO_4)_2$, silicate and oxide were used by Goldsworthy and Green (41) who found the incorporation of bentonite and lime advantageous to improve tenacity (U.S.P. 1954171, 1958102, 2004788). On the hypothesis that the hydrogen ion is the agent responsible for rendering soluble the copper of Bordeaux mixture, Sessions (42) selected the silicate as the most suitable buffer to counter acidity, adjusting its buffering power by the introduction of the ammonium ion to form complex copper ammonium silicates. The product, introduced commercially under the name Coposil (U.S.P. 2051910), also contains a small proportion of zinc ammonium silicates. A somewhat similar idea was the basis of Nikitin's work (43) upon the copper zeolites. The zeolites are complex silicates possessing base exchange properties utilized, for example, in the softening of water. The sodium zeolite of the water softener absorbs the calcium and magnesium ions from the compounds responsible for water hardness which are converted to the corresponding sodium salts. In the same way absorption of foreign bases by the copper zeolite will presumably liberate fungicidal copper compounds. Nikitin described methods for the manufacture of synthetic copper aluminosilicates by the

treatment of an alkaline sodium zeolite with copper sulphate, the excess alkalinity being neutralized with sodium hydrogen phosphate. The commercial product Z.O. is an outcome of Nikitin's work (44).

It is evident that the range of copper compounds of possible use as fungicides is inexhaustible and those apparently lacking fungicidal properties become of interest. Marsh (45) found both cuprous thiocyanate and a copper phthalocyanine relatively non-fungicidal in preliminary *in vitro* laboratory tests and the ferrocyanide failed in leaf tests. The inactivity of the ferrocyanide and thiocyanate is perhaps associated with their high inertness and insolubility while the phthalocyanine, though soluble, is extremely stable.

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Action of the Copper Fungicides on the Fungus.

As the copper fungicides are mainly used as protective fungicides, there is no need to consider separately their direct activity. The problem is reduced to the prevention of infection by spores settling on the spray-coated plant surface.

The process of the establishment of fungal infection, discussed in Chapter II, is so complicated that many ways could be suggested in which the fungicides might play an indirect part in preventing infection. Rumm (46) suggested that the more vigorous state of the sprayed vine might enable it to withstand fungal attack. Swingle (47), among many hypotheses of the mode of action of Bordeaux mixture, included the possibility that copper absorbed by the plant tissue might prevent infection either by killing the germ tube or by preventing penetration by some chemotropic influence or by interference with enzymatic processes operating in penetration.

Hypotheses based on an indirect action through the host plant fail, however, to explain the inhibition of germination of copper-sensitive fungus spores which occurs in the absence of the host plant. This action was known to Prévost (48) who showed that copper sulphate, at a dilution of 1 : 400,000, prevented the germination of " smut " spores. This high toxicity of copper in solution has encouraged many hypotheses which suggest the formation of soluble copper from the relatively insoluble copper fungicide. The solubility of the Bordeaux precipitate might, for example, be sufficient of itself to prevent germination, a hypothesis examined by Branas and Dulac (49) who concluded that, although freshly-prepared Bordeaux mixture contained enough soluble copper to be toxic to spores of *Plasmopara viticola*, the dried precipitate is too insoluble in distilled water to give toxic copper concentrations. Goldsworthy and Green (50) also obtained evidence that the Bordeaux precipitate contained a proportion of readily-soluble copper removable from the spray residue by rain water. Delage (51) also favoured this hypothesis and re-introduced the idea of cumulative action put forward by earlier workers (e.g. 52), that minute traces of copper appearing in solution would be absorbed by the spore until a toxic accumulation is eventually reached. But, even if this possibility of accumulation be accepted, the small solubility product of the relatively insoluble copper compounds now known to be fungicidal does not encourage the acceptance of hypotheses based solely on solubility in water. Most investigators have considered it necessary to look for other agencies by which copper is brought into an active fungicidal form.

Millardet and Gayon (53) observed the formation of soluble copper by the action of the carbon dioxide and slight traces of ammonium salts present in rain water and dew and noted, further, that copper appeared in solution only after the excess lime of Bordeaux mixture had been carbonated. Many investigators, in particular Pickering (54), have since accepted the view that atmospheric agencies provided a satisfactory explanation for the formation of the active fungicide. But the rôle of carbon dioxide in the fungicidal action of cuprous oxide, for example, is obscure and, even in the case of basic copper compounds, there are reasons for regarding the hypothesis as inadequate. Gimingham (55), for example, in repeating Pickering's experiments, found that the whole of the copper dissolved from the Bordeaux precipitate by the action of carbon dioxide is reprecipitated on removal of the carbon dioxide.

Gimingham therefore concluded that, although the action of excess carbon dioxide brings copper into solution, it appears impossible to assign the fungicidal activity of Bordeaux mixture to copper sulphate formed by atmospheric carbon dioxide. More recently Reckendorfer (56) has supported the carbon dioxide hypothesis suggesting that copper appears in solution as the sulphate and bicarbonate but, as Wilcoxon and McCallan (57) pointed out, since the normal cupric carbonate, $CuCO_3$, is not obtained by ordinary procedure, it is unlikely that the bicarbonate, $Cu(HCO_3)_2$, could be formed under the low carbon dioxide pressure existing in the atmosphere. The latter investigators were able to confirm the formation of soluble copper from the weathered Bordeaux precipitate and suggested that this arises through changes in composition of the adsorption complex on leaching. The removal of calcium and sulphate from the complex leaves a precipitate relatively richer in copper, the solubility of which might well be expected to increase to a point when it might become a factor in the biological activity of Bordeaux mixture.

The other agency concerned in the case of the *in vitro* action of the copper fungicides is the spore itself and the suggestion that spore excretions are involved in the fungicidal action of Bordeaux mixture was first made by Barth (58) and by Swingle (47) receiving support later from Clark (59) Ruhland (60) and Schander (61). This hypothesis was examined by Barker and Gimingham (62) who concluded that it is difficult to see how the existence of such a solvent action can be denied while McCallan (63) concluded that agents other than spore excretions are non-essential for the functioning of Bordeaux mixture. In conjunction with Wilcoxon (64) he demonstrated the presence of malic acid and of amino-acids in washings from spores of *Neurospora sitophila*. As the spore excretions are almost neutral, contrary to the suggestion of Dubacquié (65) that the solution of copper is due to acid phosphates, McCallan and Wilcoxon considered that the salts of hydroxy-acids such as malate and of amino-acids present in spore excretions, act on the Bordeaux deposit to form soluble toxic copper hydroxy- and copper amino-salts.

In practice, however, the host plant may well play a part in the mechanism of fungicidal action, either directly, or indirectly through modification of the processes concerned in *in vitro* action. Barth (58) suggested that host plant secretions might render soluble or available the copper of the spray deposit while Clark (59) and Bain (66) regarded the solution of copper by plant secretions the cause

of spray damage by Bordeaux mixture. Barker and Gimingham (62) showed that substances exuded from mechanical injuries to the leaf are capable of dissolving copper from Bordeaux precipitates, but being unable to secure leaves certainly free from previous injury, they could not decide whether soluble copper would be found on healthy leaves. De Long, Reid and Darley (67), by the examination of the action of expressed plant juices and of sugar solutions, on the Bordeaux precipitate, obtained evidence in support of the host plant excretion hypothesis, an idea on which Sessions (68) seems to have based his work leading to the development of the complex silicates as fungicides. He traced some interesting relationships between the acidity of the cell sap of the host plant and its response to the fungicide.

If it be accepted that fungicidal action follows the formation of soluble or available copper by any of three main agencies :

(1) atmospheric carbon dioxide and ammonium salts dissolved in rain water or dew,

(2) secretions from or the solvent action of the fungus,

(3) secretions from the healthy or wounded surface of the host plant,

in what forms does the fungicidally active copper appear ? In copper sulphate it seems unnecessary to look further than the cupric ion, which may also be operative with the basic copper precipitates, being derived in part from the sulphate or chloride and in part from the bicarbonate under conditions of relatively high pressure of carbon dioxide. The cupric ion would also explain the toxicity of the cuprimalates found fungicidal by McCallan and Wilcoxon (64) but, as Horsfall, Marsh and Martin (69) pointed out, the cupric ion concentration of the solutions of the copper glycine complex examined by McCallan and Wilcoxon is probably below that of equivalent cupric sulphate solutions. Yet at low concentrations the solutions of the copper-glycine complex exhibited greater fungicidal powers than the copper sulphate solutions, an indication that there exists, in the former, a material of greater inherent toxicity than the cupric ion. Indirect evidence of this possibility is afforded by observations that neither casein nor gelatine, with which copper salts combine to form the glycine type of complex, appears to reduce the field efficiency when used as a supplement of copper fungicides (70). Horsfall, Marsh and Martin (69), finding the fungicidal value of cuprous oxide to be greater than that of cupric oxide to an extent greater than could

be accounted for by other factors, suggested that the active fungicide produced from cuprous oxide may be more potent than that formed from cupric oxide. Although much of this evidence is based on preliminary observations, it is brought forward to emphasize the point that while the cupric ion is probably an active fungicide, it is not necessarily the only and most potent form of copper involved in fungicidal action.

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The Effect of Copper Fungicides on the Host Plant.

Acute Spray Damage. The drastic phytocidal activity of the water-soluble copper compounds is utilized in weed killing under which section (p. 240) the subject is discussed. But with the less soluble derivatives applied as fungicides to foliage, symptoms of acute damage may arise, starting as small purple flecks on leaves and fruit. On leaves these spots have little ill-effect unless numerous

when the intervening tissue may yellow and the leaf drop.   On some crop plants, such as peach and hop, the collapse of the injured tissue produces a " shot-hole " effect.   On fruit the killing of the epidermis at these localized areas may induce cork formation producing a " russet."   In severe cases, cracking and malformation may follow, a stage well illustrated by Moore, Montgomery and Shaw (1).

The formation of these spots has been attributed to the penetration of copper, in a soluble form, at punctures of the epidermis due to insect or fungus attack (2).   Hedrick (3) was unable to confirm this hypothesis by which apples, for example, should show a correlation between liability to copper damage and susceptibility to Scab. He observed, however, that the preliminary symptoms of Bordeaux injury arose around the stomata and at the basal cells of plant hairs.

The belief that soluble copper is the agent responsible for acute copper injury naturally led to attempts to reduce damage by the addition, to the spray, of components tending to inhibit the formation of soluble copper.   The addition of more lime to Bordeaux mixtures has frequently been recommended.   In England, the " excess lime " formula (8 : 25 : 100) has been advised (4) for use on varieties of apple to which the 8 : 8 : 100 causes injury.   The fungicidal efficiency of excess lime Bordeaux was demonstrated by Grubb (5) but a reduction of phytocidal activity was not observed either by Grubb or by Adams (6).   There is evidence that the addition of lime to copper sprays may sometimes reduce acute damage but generalizations are at present impossible on account of the possibility of lime damage and the probable contrasting effects of lime and copper derivatives on the physiological response of the host plant to spraying, subjects to be discussed below.

The use of Bordeaux mixture of low copper content, examined by Sanders and Brittain (7), was found by Moore (8) to lead to serious damage to copper-sensitive varieties of apple.   The more rational method of adding constituents countering the ill-effects of copper may not meet success until more is known of the nature of copper injury, but observations have shown that glyceride oils, added primarily to improve tenacity, tend to reduce acute damage (8, 9).

Spraying conditions may influence the extent of acute damage by copper sprays.   Hedrick (3) stated that wet weather favoured the development of injury, a statement confirmed by Howlett and May (10).   There is also evidence (11) that a heavy and blotchy

spray deposit, such as results from the over application of a poorly-wetting spray, will augment injury, a reason for the recommendation that Bordeaux mixture should be applied in limited amounts insufficient to cause drip from the foliage.

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Physiological Effects. Even when no acute injury results from the application of copper fungicides, profound physiological effects may be exerted on the plant. In part the study of these effects belongs to the general problem of the physiological response of the plant to the spray residue left by most protectant insecticides and fungicides. But as this general problem has been attacked mainly by the more specific study of the influence of Bordeaux mixture, it may be discussed alongside that of the effects peculiar to the components of copper sprays.

The importance of the general physiological effects of spray residues was first stressed by Schander (12) who attributed the differences he found between the rates of transpiration and assimilation of sprayed and unsprayed leaves to the shade effects of the spray deposit.

Early work on the effects of the spray deposit on rate of transpiration gave conflicting results (see e.g. 13–16) but, in general, favoured an increase. Butler (17) suggested that, owing to the opaqueness of the spray coating to radiation, sprayed plants cooled less rapidly than unsprayed plants and therefore transpired more fully under conditions favourable to radiation. This view was supported by the later work of Tilford and May (18) and of Kroemer and Schanderl (19). A practical application of this effect is in the reduction of " Tip-burn " of potato by spraying with Bordeaux

mixture. The browning of the tips and margins of the leaf, due in part to high temperature and in part to insect injuries (20), was found by Lutman (21) to be delayed by the application of Bordeaux mixture. It is suggested that, though the spray may result in general increase in transpiration, the opaqueness of the spray coating will smooth the transpiration curve. Though more water may be lost by the greater average transpiration, the sudden demand for water which brings about the death of the potato tissue around the water pores is lessened.

The general effect of the spray coating is to decrease carbon assimilation for, as Amos (22) suggested, the stomata are partially blocked by the spray particles. As diffusion into the intercellular spaces of the leaf is thereby decreased, less carbon dioxide is available for photosynthetic activity.

The presence of water-soluble material in the spray may increase water loss from the sprayed leaves through osmosis, a possibility investigated by Berry (23). He concluded, from the results of the application of sprays containing sucrose or calcium chloride, that desiccation by osmosis was not an important factor of spray damage. The idea that sensitivity to spray damage is correlated with a cell content of low osmotic value, adopted by Menzel (24) and by Tilemans (see 23), has not been widely confirmed by experiment; neither has the simple relationship between acidity of cell sap and sensitivity to copper or sulphur fungicides put forward by Sessions (25).

Within recent years it has been suggested that the phytocidal action of Bordeaux mixture may be due not only to the copper compounds present but also to lime. Lime injury has been differentiated from copper injury mainly by Horsfall (26). He considered that saponification of the cuticle by the lime lowers its resistance to water loss and induces a " hardening " of the leaf which prevents its normal expansion. " Hardening " of a different type may be caused by non-alkaline copper derivatives, but Horsfall and Harrison (27) pointed out that the cuticle of older leaves growing under field conditions may be resistant to saponification. It is noteworthy that, on Bordeaux-sensitive plants, it is usually the incompletely-developed leaves which show the distortion and brittleness characteristic of Bordeaux damage.

The interplay of copper and lime sensitivity is a possible explanation of the effects, observed by Blodgett and his colleagues (28), of Bordeaux mixtures of differing lime contents on potato yields.

One outcome of this work is the suggestion that, in potato spraying, it is advisable to reduce the ratio of lime in Bordeaux mixture to half that of the copper sulphate.

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Supplements for Copper Fungicides.

Early in the history of Bordeaux mixture it was found that the application of excessive amounts reduced fungicidal efficiency and increased phytocidal action. Hence it was advised (1, 2) that this spray be applied in limited amounts just insufficient to produce drip from the sprayed foliage. The reduction in fungicidal efficiency when Bordeaux mixture is oversprayed is associated with a lower spray retention, decreased tenacity and inferior coverage, points demonstrated by Hockenyos and Irwin (3). The drastic limitation of the amount of spray applied has many practical disadvantages, for it renders ineffective direct insecticides or fungicides when these are incorporated with Bordeaux mixture, increases the time taken to spray a given area, aggravates wear and tear on spray machinery and introduces the need for long lances to carry the spray to the top of the tree. It has recently been suggested (4) that the dangers of overspraying may, in part, be reduced by the use of high nozzle pressures, but a more effective method is by the modification of the physical properties of the spray

P.P.

by the addition of suitable supplements, a method investigated by
Martin (5).

It has already been suggested (p. 75) that the efficiency of
protectant fungicides, including Bordeaux mixture, is determined
by the availability of the active fungicide and its inherent toxicity
and by the amount of spray residue, its tenacity and coverage.
Supplements added to improve the latter physical qualities must
clearly neither reduce availability nor inhibit fungicidal action.
For these reasons Martin did not use casein or gelatine, supplements
recommended by Vermorel and Dantony (6), though later work (7)
indicates that the expected reduction in fungicidal value is not
realized. Nor did saponin appear suitable, for Pickering (8),
using Quillaja bark, found it unsatisfactory because of some un-
explained chemical reaction. Martin therefore experimented with
sulphite lye and with glyceride oil-Bordeaux emulsions.

The Bordeaux-sulphite lye spray proved satisfactory though it
has since been shown (7) that its tenacity is poor. Highly active
synthetic wetters also give a deposit of inferior tenacity if their
surface activity persists after the drying of the spray on the leaf.
If the supplement yields, on drying, a residue insoluble in cold
water, tenacity may be improved, probably because of better
coverage. Care is thus required in the selection of water-soluble
supplements for use with Bordeaux mixture and other copper
fungicides. Even with a supplement enhancing tenacity, initial
retention may be lowered through the better wetting properties
of the spray, an effect more apparent on foliage easily wetted by
water.

A better way of compounding a copper fungicide suitable for
application in heavy amounts is by the addition of a water-insoluble
spreader such as a glyceride oil. Martin (5) used an oil of low
free fatty acid content, e.g. edible cottonseed oil, to avoid the
formation of copper soaps. With Bordeaux mixture, moderately
stable emulsions are easily obtained without additional emulsifier.
So marked is the improvement in retention that it is possible to
reduce the copper concentration of the Bordeaux by half without
loss of fungicidal efficiency. Fajans and Martin (9), examining
the reasons for this improvement in retention, found that in the
cottonseed-Bordeaux emulsion the precipitate is partially oil-
flocculated. Preferential retention and the difficult wetting of the
water-proofed spray deposit lead to increased initial retention and
tenacity, effects which would be diminished by the incorporation

of water-soluble emulsifiers. In employing oil emulsions as supplements for copper sprays, the emulsifier concentration should be reduced to the minimum necessary for stability in the spray tank so as to obtain full advantage of the oil as sticker.

Apart from the cuprammonium derivatives, the copper sprays are all suspensions. The question of particle size thus arises and supplements may be added to prevent flocculation and aggregation or to prevent crystallization. The latter aspect is of importance in Bordeaux and other precipitated mixtures, for Bordeaux mixture loses its efficiency if kept overlong in the mixing tank. This loss was associated with the crystallization of the precipitate, a change which may be delayed by the addition of sugar, molasses or of protective colloids such as casein (10). Much work has also been done on the influence of composition and method of mixing of Bordeaux mixture on the particle size of the precipitate as judged by its rate of sedimentation (11–14). Martin (15) pointed out, however, that to assess the protective value of the precipitate on rate of sedimentation ignores the physical changes which may occur in the drying and weathering of the precipitate to form the spray deposit. The importance of degree of division in relation to fungicidal and protective value of a suspended solid unlikely to undergo physical change in the process of forming the spray deposit is apparent from the work of Heuberger and Horsfall (16) on cuprous oxides.

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Copper Dusts.

Copper preparations for application as dusts may be grouped into two categories. Firstly, there are the basic copper derivatives in finely-divided form which were introduced early in the history of the copper fungicides, e.g. David's powder. In general, dusts of this type have proved of inferior adherent properties and liable to cause damage, disadvantages which are countered, to some extent, by the addition of lime. Holland, Dunbar and Gilligan (17) found that a material more satisfactory than earlier products could be prepared by the addition, under carefully controlled conditions, of a dilute copper sulphate solution to a suspension of calcium carbonate, the particular form used being a chemically-prepared chalk described by the manufacturers as " light." The basic copper precipitate, after filtration, drying and grinding, proved suitable for use both as a dust and as a spray.

The second group of copper dusts are usually called copper-lime dusts and were originated by Sanders and Kelsall (18), whose first dusts contained arsenicals which were later omitted. Sanders (in litt. 9/1/31) was interested in the production of a form of Bordeaux which could be made by direct addition to water in the spray tank and experimented with a mixture of hydrated lime and mono-hydrated copper sulphate (see p. 125). On addition to water, however, this product curdled and he then tried the mixture as a dust. In the presence of moisture upon the plant surface, the components of the dust interact with the in situ formation of a Bordeaux precipitate. Streeter, Mader and Kokoski (19) investigated the optimum conditions of humidity for the formation of an adherent film and demonstrated the importance of applying the copper-lime dust as closely as possible to the occurrence of moisture upon the foliage.

The relative efficiencies of copper dusts and sprays in the control of potato diseases was investigated by Muskett (20), Murphy and McKay (21) and Boyd (22). Boyd found that, under field conditions, about 44 per cent. more copper per unit amount used per acre was retained by the foliage sprayed with Bordeaux mixture than by the foliage dusted with a copper-lime dust. American experience indicates that, under general conditions, the copper dusts are unable to replace sprays in the routine fungicide programme but that they are excellent supplementary fungicides for use should weather or other conditions render spraying impracticable (23). There are indications, in this country, that the copper dusts

may be of particular value for late application to tree fruit, for, at this stage, the leaves and fruit appear to be less susceptible to the phytocidal action of copper than earlier in the season.

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MISCELLANEOUS FUNGICIDES

Although a wide variety of materials has been suggested for use as fungicides, few, apart from the sulphur and copper groups, have been adopted for general use. It would be impossible to deal with the entire range of the substances proposed without degenerating into a mere catalogue, and it is intended therefore to mention only those which have found practical employment or which offer special points of interest.

It seems remarkable that protective fungicidal properties are shared, though with important differences, only by those sulphur and copper derivatives which we have just discussed. The uniqueness of the position, among the metals, of copper has provoked much comment, for it is natural to suppose that at least the related metals will show similar fungicidal properties. Wüthrich (1) found not only that mercuric chloride was more effective than copper sulphate in the inhibition of germination of fungus spores, but that ferrous sulphate, zinc chloride and zinc sulphate were also effective. Mercuric chloride, he concluded, would cause injury to the host plant and, despite its greater activity and the relative cheapness of the ferrous and zinc salts, he considered copper sulphate to be the more suitable fungicide. The organic derivatives of mercury, developed for seed treatment (see p. 267), have not found extensive use as foliage fungicides. Silver, which possesses chemical similarities to copper, was suggested by Vermorel and Dantony (2) in the form of a 0·02 per cent. silver nitrate-soap solution, as a substitute for Bordeaux mixture. Roberts and Pierce (3) found a

zinc sulphate-lime mixture successful for application to peach against *Bacterium pruni*.

The fungicidal properties of metallic salts were studied from the aspect of the Periodic Law by Wöber (4), who was able to correlate the position of copper, silver and mercury upon the atomic weight-specific gravity curve with fungicidal properties. McCallan and Wilcoxon (5), who included the non-metals in their systematic survey of the fungicidal properties of the elements, found silver and osmium compounds the most toxic and suggested that compounds of cerium, cadmium, lead, thallium and arsenic showed properties which would warrant their more extensive use as fungicides.

Mention of the fungicidal properties of cerium compounds is of interest in connection with the use of " **Perozid** " as a substitute for copper sulphate in Germany during the 1914–18 war. Perozid, a residue from gas-mantle manufacture, is a mixture of the sulphates of the cerium group of rare earth metals. It was first used by Appel (6), and Wöber recorded that the general experience was that the 3 per cent. spray approached the 1 per cent. Bordeaux mixture in fungicidal efficiency only in years of slight attack or in dry regions. Perozid has not survived the re-introduction of cheaper copper sulphate.

The fungicidal properties of **arsenical compounds** has an important bearing upon the properties of certain combined insecticides-fungicides (see p. 231). That lead arsenate possesses fungicidal properties appears to have been first observed by Waite (7), whilst Morse (8) claimed that arsenate of lead paste controlled Apple Scab as well as did Bordeaux mixture or lime sulphur. Whetzel, McCallan and Loh (9) found calcium arsenate of promise for the control of *Alternaria* sp. In trials upon the Hop Powdery Mildew, Salmon and Horton (10) found that the soluble arsenates are highly toxic. In a continuation of this work, Goodwin, Martin and Salmon (11) showed lead arsenate to be considerably less fungicidal than disodium arsenate or dicalcium arsenate, but that solutions of lime sulphur and lead arsenate below fungicidal strength, when mixed together, were fungicidal. This result was ascribed to thioarsenates, which were found to have marked direct fungicidal properties but, owing to their higher solubility, the danger of phytocidal activity is greater than with the arsenates. Dilute solutions of arsenite or arsenate of soda were employed with success by Garbowski and Leszczenko (12) for the control of American Gooseberry Mildew and by Szembel (13) against Cucumber Powdery Mildew.

The use of **potassium permanganate** as a fungicide has often been suggested, notably by Guozdenović (14), who advocated its addition to Bordeaux mixture. He found this spray to be effective against both the Powdery and Downy Mildews of Vine, and this combined fungicide has been recommended in New Zealand (15). An important difficulty in the employment of potassium permanganate as a spray constituent is its ready decomposition in the presence of organic matter. It is presumably to its oxidizing properties that its fungicidal action is related, and, in contact with leaf and fungus, its rapid decomposition will not permit it to play any rôle as a protective fungicide. This decomposition interferes with the preparation of the permanganate-Bordeaux mixture. The copper sulphate solution is usually prepared in a wooden receptacle but, if permanganate be added, the wood may cause its decomposition. More serious, however, is the difficulty of finding, for use with permanganate, a suitable spreader, the importance of which in the case of the direct fungicide has already been emphasized. The entire list of organic spreaders react with permanganate. Guozdenović employed either lime or Bordeaux mixture to improve adherence, whilst Vermorel (16) found that the addition of silicic acid sols, proposed by Degrully (17) as spreaders, caused injury.

The **alkali carbonates** were found of value against American Gooseberry Mildew by Dorogin (18) and washing soda ($Na_2CO_3.10H_2O$) has been used with success both in Holland (19) and in England (20), particularly upon sulphur-shy varieties of gooseberry. In the latter case, the value of washing soda was found to be greatly impaired by rain after application. It is probable that fungicidal activity is associated with the alkalinity of the solution. Martin and Salmon (21) showed that solutions of sodium carbonate, hydroxide and sulphide had similar fungicidal properties to the Hop Powdery Mildew but that all were highly phytocidal to hop foliage, the least injurious being sodium sulphide.

Compounds of the metals were found, by McCallan and Wilcoxon (5), to exhibit fungicidal properties independent of the acidic radical of the compound used. In the case of compounds of non-metals, however, the toxicity of different derivatives of the same non-metal varied widely. In particular, the volatile hydrides were highly toxic, a feature of interest in connection with the fungicidal activity of **selenium,** an element which, because of its close relationship to sulphur, might be expected to possess fungicidal properties. Wilcoxon and McCallan (22) found that selenium and

tellurium were far less toxic than sulphur to the fungus spores tested although hydrogen selenide appeared to be of the same order of toxicity as hydrogen sulphide (see p. 108).

Of the organic derivatives, the **oils** have attracted attention for fungicidal purposes, mainly on account of their excellent spreading properties. Kerosene emulsions were used by Halstead and Kelsey (23) and, for the control of American Gooseberry Mildew, by Barker and Lees (24). The latter workers had concluded that to be effective the spray would have to wet the fungus thoroughly and they had found soft soap solutions deficient in this respect. The success of the paraffin-soft soap emulsion in wetting the fine waxy threads secreted by the woolly aphis suggested its trial against the fungus. Although the 2 per cent. emulsion was found to cause but little foliage damage, it did not suffice to protect the sprayed plant from re-infection. The introduction of highly-refined lubricating oils as insecticides (see p. 202) which may be applied to foliage, has resulted in tests of their action upon fungi. McWhorter (25) found one such product successful against Rose Powdery Mildew (*Sphærotheca pannosa* (Wal.) Lév.). The relative non-volatility of the oil would suggest that this fungicidal action may be solely protective, though McWhorter considered the spray possessed a direct toxic action. This conclusion is supported by the work of Martin and Salmon (26), who found that emulsions of highly-refined petroleum oils were effective against Hop Powdery Mildew. Under certain conditions, however, the oil emulsions caused foliage damage, and Martin and Salmon showed that vegetable oils were less phytocidal and more fungicidal than the petroleum oils. Later Martin and Salmon (27) proved that direct fungicidal activity to *S. humuli* was a property common to the glyceride structure and hence shared by all animal and vegetable oils. Castor oil, a glyceride of the hydroxylated fatty acid, ricinoleic acid, proved less effective. The high degree of correlation between instability of the emulsion and its fungicidal efficiency is of interest in connection with the influence of the type of emulsion upon the insecticidal efficiency of petroleum oils (see p. 208).

Soaps, which are chemically related to the glyceride oils, have found use against *Botrytis* sp. (28, 29). The marked lytic action of surface active substances, such as soaps and saponin, upon fungal zoospores, was observed by Goodwin, Salmon and Ware (30), who suggested that soap dusts may be of practical value as fungicides in cases where rapid but not persistent protective action is required.

A survey, on systematic lines, of the spray properties of organic solvents and related products which are now synthesized on a commercial scale, was begun by Martin and Salmon (31) employing Salmon's technique for the evaluation of direct fungicidal properties. Although·no promising fungicides, apart from the glyceride oils and the naphthols, were found, pointers were obtained to possible generalizations. Thus the high phytocidal properties of certain aromatic compounds were not apparent in the corresponding hydrogenated products ; the alcohols, as a class, proved inert, but phytocidal properties were exhibited by the glycols. Pastac (32) also showed that the fungicidal properties of the naphthols were greater than those of the phenols and he showed that sulphonation caused a marked decrease in fungicidal activity.

The suggestion that the fungicidal action of sulphur may involve a reaction akin to the combination of sulphur and the rubber molecule as in vulcanization (33) was followed by an examination of the fungicidal properties of rubber accelerators (34). Of these compounds the thiuram sulphides were found to be weakly fungicidal, **Tetra-methyl thiuram disulphide**—which, it may be noted, resembles a polysulphide in possessing a sulphur atom in excess of the monosulphide—showing promise in field trials against Apple Scab (35).

The fungicidal actions of synthetic organic compounds developed primarily as insecticides were investigated by Wilcoxon and McCallan (36) who selected, as of promise, certain organic thio-cyanates (see p. 222) and alkyl resorcinols. Marsh (34) did not find lauryl thiocyanate effective whilst thiodiphenylamine (see p. 173), though moderately fungicidal in *in vitro* tests (37), failed in leaf tests. The use of highly halogenated and nitro-derivatives of aromatic hydrocarbons as constituents of the proprietary fungicides Folosan (pentachlornitrobenzene) and Brassisan (trichlordi-nitrobenzene) (38) is noteworthy in connection with the earlier trials of similar but less substituted derivatives for soil treatment (see p. 282).

Perhaps the most comprehensive survey of fungicidal properties yet carried out has been the work of Morris (39) and of Fargher, Galloway and Probert (40) at the Shirley Institute. The purpose of this survey was the discovery of antiseptics suitable for the protection of textile fabrics from mould fungi. Fungicidal efficiency was determined by the concentration necessary to prevent the growth of saphrophytic fungi upon flour paste. Their results

showed that, in general, the toxicity of phenolic derivatives was increased by the introduction of alkyl, nitro or halogen groups and was decreased by the introduction of acrylyl, sulphonic acid or additional hydroxyl groups. Acetanilide was found to be about half as toxic as phenol and a survey of the anilides revealed the high fungicidal activity of the salicyl derivative. Further, these investigators recorded that **salicylanilide** appeared to be non-phytocidal. The product, under the trade name " Shirlan," has since been applied to plant protection purposes. Bewley and Orchard (41) obtained successful control of Tomato Leaf Mould (*Cladosporium fulvum*), and of certain powdery mildews by the repeated application of sprays containing salicylanilide with Agral 1 as the spreader. Martin' and Salmon (31) found salicylanilide to have but little effect upon the Hop Powdery Mildew when applied with Agral 1, but obtained greater action when this non-alkaline spreader was replaced by soap and when the water-soluble sodium salt of salicylanilide was used. Their results suggested that Shirlan preparations are effective in killing the Hop Powdery Mildew at one application only under conditions when a high proportion of the salicylanilide is in solution.

The application of **dyestuffs** as fungicides has been investigated, mainly in France by Truffaut and his colleagues (42), who have found certain auramines and phosphines efficacious against powdery mildews. Among points of interest in this work are the inefficiency of Phosphine ACR when tested by *in vitro* methods as contrasted with its high activity against vine mildew when in contact with the leaf or fungus, and the generalizations, deduced by Pastac (43), concerning fungicidal activity and molecular structure. He showed, firstly, that activity increased with molecular weight up to a maximum and then fell rapidly when the molecule is presumably too large to pass readily through the cell wall, secondly, the marked reduction of toxicity following sulphonation and, thirdly, the increased activity which follows the alkylation of certain amino-compounds. Thus dimethyl aniline was found to be more toxic than aniline and Violet 5BO was more fungicidal than Fuchsine. In this country, Bennett (44) has successfully controlled the Fusarium Patch Disease of bowling and golf greens by watering the turf with dilute solutions of malachite green.

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CHAPTER VII

INSECTICIDES—STOMACH INSECTICIDES

The materials employed for application to the plant against insect pests have been classified into two groups according to their mode of action. The most widely used of the first group—the Stomach Insecticides—are the arsenicals.

THE ARSENIC GROUP

Although arsenic was known long ago to be poisonous to insects, its use as an insecticide only became general about the middle of the last century. In France, the use of arsenicals for the destruction of insects was prohibited by the French Ordinance of 1846, Article 10, but so successful was their employment in the United States that their reintroduction into Europe was inevitable.

The more important of the arsenical compounds which have been used as insecticides are considered below in an historical order, the discussion of the general features of their action upon the insect and upon the plant being reserved until later.

Paris Green. Following the appearance of Colorado Beetle in the eastern parts of the United States during the first part of the nineteenth century, desperate remedies were tried, and in 1867 Markham (1) found in Paris Green, an arsenical pigment, a successful means of control. In 1872 Le Baron (2) used this material against the canker worm, and it was in repeating these experiments in 1878 that E. P. Haynes observed that Paris Green simultaneously controlled the Codling Moth (*Cydia pomonella* L.). In such a manner was the use of Paris Green as an insecticide established.

The main constituent of Paris Green, known in Germany as Schweinfurter Grün, and also called Emerald Green, French Green and Mitis Green, is a complex compound of copper acetate and copper arsenite of formula $(CH_3COO)_2Cu.3Cu(AsO_2)_2$. The material available for insecticidal purposes, made originally from the variable raw material verdigris was far from constant in composition.

Avery (3), in an examination of specimens of Paris Green prepared by different methods, found that the precipitate consisted of compounds of copper meta-arsenite and copper acetate combined in a ratio usually nearly 3 : 1 but sometimes approaching 2 : 1. The variable nature of the older Paris Greens was also shown by Van Slyke and Andrews (4). The methods of manufacture of Paris Green have since become more standardized. Further, the older Paris Greens were inferior in degree of fineness, an important point in spraying, for the finer the particles the better the suspension.

To distinguish the improved commercial products, the older name of Schweinfurter Grün, which had become associated with an inferior insecticide, has been abandoned in Germany in favour of such trade names as Uraniagrün, Silesiagrün, Titaniagrün, Frukusgrün, St. Urbansgrün, and Elafrosin. The specification proposed by Hilgendorff (5), to which these products conform, requires a definite degree of fineness and limits the water-soluble arsenic to below 3·5 per cent. expressed as arsenic trioxide. The product must also contain at least 55 per cent. total arsenic oxide, at least 30 per cent. cupric oxide and at least 10 per cent. acetic acid.

Copper aceto-arsenite, the main constituent of Paris Green, is readily decomposed. Avery and Beans (6) showed that even the purest sample available breaks down on treatment with water to form water-soluble arsenic. Further, Holland and Reed (7) showed that arsenic goes into solution on treatment with either carbon dioxide or ammonia. This ready hydrolysis is, as will be shown later, the most objectionable feature of an excellent insecticide.

Dearborn (8) has examined the chemistry of the fatty acid homologues of Paris Green. The compounds he has described (U.S.P. 2104584, 2127384) and the basic cupric arsenate patented by Klumpp (U.S.P. 2112102) and described by Witman et al. (9), are of special interest as they may combine protective fungicidal properties with insecticidal properties.

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London Purple. In view of the success of Paris Green against the Colorado Beetle, an arsenical residue from the manufacture of magenta was sent in 1878 by Hemingways & Co., a London firm, to C. E. Bessey, an American entomologist, for trial as a substitute. The material proved successful and was given the name London Purple.

The active principle is here arsenite of lime together with some arsenate of lime. The material often contained a higher percentage of arsenic than Paris Green, but proved so variable in character that its use as an insecticide ultimately went out of practice.

Between the years 1868 and 1892, the date of the first use of lead arsenate, a number of other arsenicals were tried as substitutes for Paris Green. Products similar in nature to London Purple, such as Paris Purple and the arsenite of copper known as Scheele's Green, met with no marked success. It was, however, realized that the successful arsenical would be of more constant composition and would give rise less easily to soluble arsenic, in the form of arsenite or arsenate, to which the foliage injury was attributed. Work in this direction finally led to the introduction of lead arsenate.

Lead Arsenate. This arsenical was first employed by Moulton in 1892, who, experimenting on the control of the Gipsy Moth (*Lymantria dispar*) proposed the precipitation of arsenate of soda by lead acetate in order to obviate the foliage injury caused by the soluble arsenic. Tests with this material, to which the name " Gypsine " was given, were reported by Fernald (10) and subsequent workers spoke so favourably of the new spray that it soon became established as the arsenical approaching most nearly the ideal.

The lead arsenates most commonly employed for insecticidal purposes and described in America as " acid " lead arsenates, approximate in composition to the diplumbic hydrogen arsenate $PbHAsO_4$. This compound is a comparatively stable compound almost insoluble in water, and though containing the heavy lead atom the precipitate remains well in suspension. Although McDonnell and Graham (11) have shown that hydrolysis of the diplumbic salt, with the formation of soluble arsenic and a more basic lead arsenate, can occur, reports of spray injury due directly to this hydrolysis are rare.

In the United States, lead arsenates of a more basic nature have been employed under the name of neutral or " basic " lead arsenates, or triplumbic arsenate (T.P. arsenate). It was at one time considered that the triplumbic ortho-arsenate $Pb_3(AsO_4)_2$, was the main constituent of such products, but the work of Robinson and Tartar (12) and Streeter and Thatcher (13) has shown that the compounds present are members of a series of ill-defined basic arsenates.

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Calcium Arsenate. Although the use of lead arsenates as insecticides has met with the greatest success, the lead appears to play no important rôle. The desirability of the replacement of the lead by a lighter and less poisonous metallic radical led to the commercial production of calcium arsenates free from water-soluble arsenic.

Apart from London Purple, arsenites of lime had previously been suggested and used as insecticides in 1889 by Gillette (14), and independently recommended by Kilgore (15). Owing to many cases of foliage injury it never became of importance. The history of the use of arsenate of lime as an insecticide is not known, but Pickering (16) stated that it had been in use in the United States prior to 1907.

The chemistry of the calcium arsenates is in many ways similar to that of the lead arsenates. It was at one time thought that besides the dicalcium hydrogen arsenate $CaHAsO_4$, there existed a definite tricalcium salt $Ca_3(AsO_4)_2$. In repeating the methods given by Robinson (17) for the preparation of these two compounds, Goodwin and Martin (18) found that, whereas the dicalcium hydrogen arsenate may be prepared easily and well as the crystalline monohydrate $CaHAsO_4.H_2O$, the preparation of the tricalcium salt presented difficulties. They showed that, as with the lead arsenates, there is probably a continuous series of basic calcium arsenates formed and that no definite break corresponding to one definite basic arsenate is shown. Clifford and Cameron (19) also concluded, from phase rule studies, that there is no evidence that tricalcium

arsenate can be formed from, nor persist in contact with, aqueous solutions.

With the lead arsenates, the material in general use as an insecticide consists mainly of the diplumbic hydrogen arsenate. With the calcium arsenates, however, the dicalcium hydrogen arsenate is too soluble for safe application to the foliage. The commercial calcium arsenates are therefore prepared so as to contain an excess of lime. Those examined by Cook and McIndoo (20) were all more basic than the tricalcium arsenate. Such preparations may be considered to consist of mixtures of indefinite basic calcium arsenates and calcium hydroxide, which on exposure will yield calcium carbonate.

A further important difference between the lead and calcium arsenates employed as insecticides is that whereas the lead arsenates are relatively stable and undergo but little change after application to the foliage, the basic calcium arsenates suffer decomposition. Goodwin and Martin showed that the basic calcium arsenates are hydrolysed in aqueous suspension, yielding calcium hydroxide which, after spraying, will be reprecipitated as calcium carbonate. The ultimate result is a slow transformation of the basic calcium arsenates to dicalcium hydrogen arsenate and calcium carbonate. Thus the solubility of the dicalcium salt is temporarily reduced by the addition of lime, to which is due the increased freedom from spray injury of those commercial calcium arsenates in the manufacture of which excess lime has been used.

It is of interest to reflect upon the relative values of the lead and calcium arsenates as insecticides. The lead arsenates, as we have seen, form admirable spray suspensions, still further improved by the use of a suitable protective colloid. The dried lead arsenates, however, do not reform the excellent suspensions given by the paste. The basic calcium arsenates, on the other hand, yield, when properly dried, an excellent powder which has found an important application as a dust, notably for use against the Cotton Boll Weevil (*Anthonomus grandis* Boh.) (21). The lead arsenates are therefore of greater value as sprays, the calcium arsenates as dusts.

Without regard to the relative efficiency of the two materials as insecticides, other considerations would point to a greater economy with the use of calcium arsenates. The dried calcium arsenates contain on the average 40–45 per cent. arsenic oxide (As_2O_5), the dried lead arsenates only 31–32 per cent. arsenic oxide, a figure which must be reduced, for the commercial pastes contain from

40–50 per cent. of water. Further the calcium arsenates do not contain the more costly and heavier lead of the lead arsenates, which, with the water they contain, adds greatly to their transit costs. Finally, when the question of poisonous spray residues arises, preference is usually given to the calcium arsenates because of the cumulative poisonous properties of lead compounds.

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Miscellaneous Arsenicals. Attempts to use **arsenious oxide** (white arsenic) direct as a spray insecticide have met with little success. Although the oxide is not readily soluble in cold water, solution is sufficiently rapid in the presence of impurities likely to be present in tap water or on the leaf surface to produce severe foliage damage. It is probably because of a rather unusual absence of such factors that reports are to be found of the successful use of arsenious oxide without injury to the plant (22).

Of the commoner arsenicals tried by Volck and Luther (see 23), at the California Experiment Station, zinc arsenite was recommended for general use. It appeared on the market for a while but, in other localities, caused severe spray damage (24). Its ready decomposition by carbon dioxide to liberate soluble forms of arsenic was demonstrated by Schoene (25).

In 1919, Patten and O'Meare (26) reported unsuccessful trials of magnesium arsenate, made by a process then recently patented (U.S.P. 1344018). Later patents (U.S.P. 1420978, 1466983 : B.P. 251330) were the results of attempts to prepare magnesium arsenates safe for foliage application. The physical and chemical properties of products made by these processes were examined by Dearborn (27) but it would appear (see 28) that there is risk of spray damage even with these forms of magnesium arsenate.

The white deposit left by lead and calcium arsenates is objectionable on tobacco foliage, for it resembles mould and reduces the market value of the leaves. The incorporation of dyestuffs or pigments was not found wholly successful and the product " **Manganar** "

has been placed on the market for use in such cases. This product is manufactured under patent from pyrolusite and white arsenic in the presence of oxidizing agents. The mixed manganese arsenates so formed are mixed with lime, and burnt umber may be added as a diluent, the final product containing approximately 40 per cent. arsenic pentoxide, 32 to 40 per cent. manganese oxide and about 16 per cent. lime. The general conclusions of trials reviewed by Dearborn (29) is that Manganar is not as effective an insecticide as lead arsenate.

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Action of Arsenicals upon the Insect.

The relative efficiency of an arsenical depends primarily upon the amount of arsenic present. In the arsenicals which have, up to the present, found employment as insecticides, the arsenic is present either as arsenite or arsenate, i.e. as trivalent or pentavalent arsenic. Against insects, Cook and McIndoo (30) were unable to find any noteworthy difference in the toxicity of arsenite and arsenate of the same base and of equal arsenic content, but Campbell (31) showed that, against the Tent Caterpillar *Malacosoma americana* F., trivalent arsenic is the more toxic. This result has been confirmed by Fink (32) and by Fulmek (33), of whom the former concluded that arsenious acid is 57 per cent. more toxic than arsenic acid and that sodium arsenite is 59 per cent. more toxic towards the insects he tested. Fink based his figures upon the depression of the oxygen consumption of the poisoned insect. His study of the effect of arsenicals upon the respiratory metabolism of the insect led to the conclusion that they induce an inactivation of the oxidizing enzymes, perhaps by an interference with the normal functioning of glutathione in the oxidation-reduction phenomena of the cell tissue.

This hypothesis of the mode of action of arsenic is similar to that advanced to account for. the trypanocidal action of organo-arsenic

derivatives. Thus Cohen, King and Strangeways (34) concluded that there is a remarkable affinity between arsenic and organically-combined sulphur. They suggested that the toxic action of arsenic is due to a chemical reaction involving thiol groups and, possibly, glutathione in particular. " It would be premature to attribute this action to a direct effect on respiration controlled by glutathione, as there is no consensus of opinion at the present time on the real function of glutathione in living processes."

The second factor which determines the relative efficiency of arsenicals is the base present. In comparative tests upon the Colorado Beetle, Wilson (35) found that Paris Green has the greatest killing efficiency of the arsenicals in general use ; ordinary brands of arsenate of lead, zinc arsenite and calcium arsenate were a trifle slower in action. Cook and McIndoo (30), from a series of careful experiments on a wide range of insects, arrived at the following conclusions : Paris Green is more toxic than zinc arsenite ; acid lead arsenate is more toxic than basic lead arsenate, but on equivalent arsenic contents Paris Green is no higher in toxicity than acid lead arsenate.

As a working hypothesis it may be taken that the relative toxicity of an arsenical is closely related to its chemical instability. The easy hydrolysis of Paris Green is coupled with a high relative toxicity, the most stable basic lead arsenates have a relatively poor killing efficiency. In Paris Green the arsenical is rapidly decomposed in the insect intestine, yielding soluble arsenic capable of absorption, whereas with the basic lead arsenate the material passes unchanged from the insect body in the excreta.

This hypothesis has been examined by Fulmek (33), who found the order of toxicity of metallic arsenites to a number of species of caterpillars to be of the order : magnesium, lead = calcium = copper, iron and zinc ; the metallic arsenates being of the order : lead, copper, calcium, magnesium, zinc and iron. The arsenites proved more toxic than the arsenates and the order of toxicity of the latter ran roughly parallel to their solubilities in buffer solutions of pH 9·0, which is approximately that of the digestive juices of the insects. Work upon the hydrogen ion concentration of the insect intestine has been surveyed by Uvarov (36) and variations are shown according to insect species and part of gut examined. Trappmann and Nitsche (37), for example, found the mid-gut of representative species of insects to be of pH 7·58–9·07. Swingle (38) obtained evidence of a wider range, from pH 5·9 to 9·6, and

of the importance of phosphates in controlling the solution of arsenic by the more alkaline digestive secretions, especially from lead hydrogen arsenate. He attributed the decomposition to the precipitation of lead as lead phosphate. The relative toxicities of lead hydrogen arsenate, calcium arsenate and magnesium arsenate towards nine species of leaf-eating insects was correlated with the relative amounts of soluble arsenic formed from these arsenates in phosphate buffer solutions of the hydrogen ion concentration found in the mid-gut of these insects. The solubilities of the three arsenates was approximately equal in phosphate buffer solutions of pH 6·0–6·5 ; in more alkaline solutions, lead hydrogen arsenate was more soluble than the magnesium arsenate ; in more acid solutions, the magnesium arsenate was more soluble than the lead arsenate. In a parallel manner, the lead arsenate was more toxic than magnesium arsenate to larvæ with alkaline mid-guts, e.g. *Protoparce sexta* Johan., while magnesium arsenate was more toxic than the lead arsenate to larvæ of acid reaction in their mid-gut, e.g. *Epilachna varivestis* Muls.

The possibility of devising a solubility test, similar in principle to the determination of " available " phosphate in phosphatic fertilizers, to determine the toxicity of a commercial arsenical deserves consideration. The subject has been reviewed by Borchers and May (39) and by Trappmann and Nitsche (37). The latter were sceptical of the value of such laboratory tests, for the practical worth of an arsenical will be determined, not only by its inherent toxicity, but by those other physical properties such as adhesiveness to foliage which influence its protective qualities. Further, it is possible that impurities present in commercial products may affect biological performance by deterrent or emetic properties. Thus O'Kane (40) mentioned the case of the Japanese Beetle (*Popillia japonica* Newm.), a pest notoriously difficult to poison with arsenicals which appear to act more as deterrents. By mixing with the spray an intestinal sedative such as bismuth subcarbonate, more of the poisoned leaves were eaten and a greater kill secured. Then again, the insect may vomit the irritant poison, as shown by Cook and McIndoo (30), who recorded that for honey bees, which voided none of the arsenical eaten, the fatal dose of arsenic was about six times less than that of the silkworm, which voided 90 per cent. of the amount eaten.

The effect of sub-lethal doses of an arsenical upon the insect is of interest, for Friedericks and Steiner (41) and Voelkel (42) observed

that the larvæ of certain moths, when not killed, produced females of impaired fertility.

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Action of Arsenicals on the Plant.

Injury to foliage by arsenical sprays or dusts first appears as a wilting followed by a browning and shrivelling of the tissue often with interveinal necrosis. This damage was attributed to water-soluble arsenic compounds and Swingle, Morris and Burke (43) subdivided the arsenicals they tested into the " soluble " and there-fore phytocidal class and the " insoluble " class, e.g. lead arsenate, zinc arsenite. Owing to variance between different samples of the " insoluble " class, they gave no generalization on the relative " safety " of these arsenicals though it was realized that the presence of water-soluble arsenical compounds in these products was a cause of spray damage. Early in the history of lead arsenate, restrictions were imposed on the content of water-soluble arsenic and the same test has been applied, with equal or less success to other arsenical compounds of the " insoluble " class. With the calcium arsenates, the direct estimate of water-soluble arsenic proved an unreliable indication of phytocidal properties and, following up earlier work by Kelsall and Herman (44), Pearce, Norton and Chapman (45) devised a chemical test for the " safeness to foliage " of commercial calcium arsenates involving a preliminary carbonation of the free lime present.

Another corollary of the observation that phytocidal properties are associated with water-soluble arsenic is the attempt to reduce the latter by precipitation with " correctives " such as lime. Swingle, Morris and Burke concluded that lime restrains to some

extent the injurious effects of calcium arsenite and Paris Green. It has been shown (46) that lime added to the calcium arsenates precipitates the soluble arsenic as basic calcium arsenates which slowly yield soluble arsenic under the influence of carbon dioxide.

The interactions of free lime and the more insoluble arsenicals are less simple. Campbell (47), investigating the cause of severe arsenical injury by acid lead arsenate to which lime had been added, concluded that an interaction occurred resulting in the formation of basic lead arsenates and basic calcium arsenates. The latter compounds, on exposure, gave rise to the dicalcium arsenate, yielding more soluble arsenic than the original lead arsenate. On the other hand, trials by Van der Meulen and Van Leeuwen (48) showed that the addition of slaked lime to lead arsenate prevented injury to peach foliage. They showed, by laboratory experiments, that the reaction between the calcium hydroxide and the diplumbic hydrogen arsenate results in a complete decomposition of part of the latter to form lead hydroxide and basic calcium arsenates. The reaction is however too slow to produce an amount of soluble arsenic sufficient to cause injury.

Correctives added to lessen arsenical injury by reducing the tendency to form water-soluble arsenic have been discussed by Ginsburg (49). In trials made by Goodwin and Martin (50), it was observed that Bordeaux mixture appeared to be a more effective corrective than lime. This observation was confirmed by Moznette (51) in the case of Paris Green and calcium arsenate and by Parfentjev and Wilcoxon (52) for calcium arsenite.

Arsenical damage may arise through the presence, in the water used for spraying, of compounds reacting to form soluble arsenic. Ginsburg (53) found that hard waters rich in bicarbonates reacted with lead hydrogen arsenate to form water-soluble arsenates. With such waters, an anomalous situation appears for Ginsburg found that the addition of soap, a spreader not generally recommended for lead arsenate because of interaction to produce soluble arsenates, reduced the tendency to spray damage through the preliminary precipitation of the soap by the hard water, the insoluble soap preventing the interaction of lead arsenate with the alkali carbonate simultaneously formed.

Biological factors also appear in the causation of arsenical damage. Thus Patten and O'Meara (54) suggested that the carbon dioxide given off by the leaves may give rise to soluble arsenic, especially from calcium arsenates. The dew collected from cotton foliage

was shown by Smith (55) to contain relatively large quantities of salts favouring the formation of soluble arsenic from calcium arsenate. Swingle, Morris and Burke (43) noted that the injury to the foliage occurs via the lower epidermis regardless of the number of stomata on the two surfaces. This would indicate a direct penetration of the thinner cuticle as distinct from the stomatal penetration of the sulphur sprays.

Lastly, the question of arsenical injury is complicated by the influence of climatic conditions. No conclusions have yet been arrived at as to the general manner of this action, but Fernald and Bourne (56) have shown that abnormal weather conditions produce more severe injury. It would appear that high humidity and high temperature are the optimum conditions for arsenical injury. Strachitzkii (57) suggested that a greater susceptibility to injury may be expected in rainy seasons because of the poorer development of cuticle.

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Supplements for Arsenical Insecticides.

In common with protective fungicides, the arsenical insecticides depend, for efficiency, on the initial amount and tenacity of the spray residue and on its degree of coverage. The addition of supplements to improve these properties was not at first practised, but soaps have been and are still sometimes recommended, in spite of their interaction with the arsenical to produce water-soluble arsenic compounds. Cook and McIndoo (58) showed that, by

admixture with fish-oil soap, the whole of the arsenic of lead hydrogen arsenate is, after standing one day, rendered soluble with the formation of lead " soaps."

Lime casein was, at one time, frequently recommended and the free lime present will function as a corrective for injury from the more soluble arsenic compounds. It was, however, the more uniform coating of spray deposit which prompted the recommendation of lime casein by Lovett (59). Field trials did not confirm the suggestion that the addition of lime casein would enhance the insecticidal efficiency of lead arsenate. Smith (60) found that the complete covering of the surface of the apple fruitlet did not prevent attack by Codling Moth and that an important factor was the amount of arsenate per unit area of plant surface to be protected. The improvement in coverage obtained by the use of lime casein was, in effect, outweighed by the decrease in initial retention. The supplement required is one which will improve retention and tenacity without loss of coverage.

For the enhancement of the tenacity of lead arsenate sprays, petroleum oil emulsions were found of promise by Lovett. Spuler (61), who examined the effect of adding various types of petroleum oils to lead arsenate sprays against Codling Moth, found that, in one case, the combination of high-boiling petroleum oil and lead arsenate was as effective an insecticide as a spray containing four times the amount of lead arsenate alone. The increased difficulty of arsenical residue removal when applied in combination with oils has frequently been reported.

The use of glyceride oils as stickers for lead arsenate was suggested by Hood (62), who selected a refined fish oil for recommendation, emulsifying the oil by agitation with lead arsenate paste. The stability of the emulsion so prepared when petrolem oils are substituted for the glyceride oil is probably insufficient to ensure uniform application. Further, petroleum oils are found to cause a flocculation of the lead arsenate suspension (61), a disadvantage overcome by the addition of lime casein or other spreaders which act as deflocculators probably through their ability to function as emulsifiers. The relative merits of fish oil and petroleum oil were examined by Webster and Marshall (63) who also noted that tenacity was improved by the addition of oleic acid to the oils. From this work was evolved the so-called " inverted " spray mixture (64) in which advantage is taken of preferential retention (see p. 93) to build up a spray load of oil-flocculated residue of high tenacity.

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THE FLUORINE GROUP

Sodium fluoride is an old-established cockroach poison which, according to Fulton (65), is not less toxic towards the earwig *Forficula auricularia* L. than arsenious oxide. Ripley (66) recommended its use as a substitute for arsenicals in poison baits. Unfortunately, as it is moderately soluble in water, the risk of spray damage and rapid removal by rain prohibit its use upon foliage. As sodium silicofluoride (sodium fluosilicate, Na_2SiF_6) is of but slight solubility in cold water, Marcovitch (67) recommended its use instead of sodium fluoride for application to the plant. Marcovitch also found calcium silicofluoride and cryolite (sodium aluminofluoride, Na_3AlF_6) successful as dusts. His claim was substantiated by Gimingham and Tattersfield (68), who tested suspensions of sodium and potassium silicofluorides as insecticides.

The silicofluorides, or better from the view-point of chemical nomenclature, silicifluorides, are of great value as antiseptics. Against insects it is accepted that they act as stomach poisons, though their action may in some cases be primarily due to contact. Shafer (69) suggested that sodium fluoride adhering to the legs of the cockroach might cause irritation ; the insect to rid itself of the irritant draws its legs through its mouth parts, whereby the poison reaches the alimentary system. The effect of the fluorides upon the insect intestine was examined by Pilat (70).

An early difficulty encountered in the use of silicofluorides as sprays or dusts was their high apparent density. Thus Walker and Mills (71) found that sodium silicofluoride was more toxic than calcium arsenate to the Cotton Boll Weevil *Anthonomus grandis* when compared on a volume basis, but two to four times the weight of silicofluoride was required to cover effectively the area treated with calcium arsenate. Barium silicofluoride and cryolite proved

only slightly less effective than calcium arsenate, but the weight required per acre to give comparable results was greater.

The disadvantage of the high apparent density of natural cryolite was found to be less serious with the synthetic product, the practical trials of which have been reviewed by De Long (72). Barium silicofluoride proved unduly corrosive to spray pumps and valves, a disadvantage which could be corrected by the addition of a small proportion of a more soluble fluoride. This discovery (U.S.P. 1,931.367) has been utilized in the product "Dutox," which is stated to contain 72 per cent. barium silicofluoride, 8 per cent. sodium aluminofluoride and 20 per cent. inert constituents.

The development of the fluorides as insecticides has been arrested by the discovery that fluorine compounds, although not possessing the acute toxicity to warm-blooded animals of the arsenicals, have serious deleterious effects. The presence of traces of fluorine compounds in drinking water has been shown to produce mottling of the teeth. Smith and Leverton (73) found that the amount of fluorine required to cause initial damage to rat incisors is so small that differences in the solubility of the fluorine compound used was not a factor. The harmlessness of the fluorine insecticides to stock and man is therefore in question.

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MISCELLANEOUS STOMACH INSECTICIDES

The need for stomach poisons of low toxicity to warm-blooded animals has provoked much investigation. Of plant products, rotenone and the related insecticides have been found by practical trial to be most effective and their ability to function as stomach poisons has been established by laboratory trial (74, 75). Nicotine salts, such as the tannate, oleate and sulphate, have also been

shown to act via the alimentary system, but as these two groups of products possess contact insecticidal properties of wider practical use, they are described in the next chapter.   The ground rhizome of White **Hellebore** (*Veratrum album* L) was employed as far back as 1842 (76) against Gooseberry Sawfly *Nematus ribesii* Scop. Hellebore powder, on exposure to air, loses its poisonous properties and it is therefore of special usefulness for the treatment of fruits, such as gooseberry or currant, at a period too near maturity for the application of arsenicals.   This instability of the effective constituents is a disadvantage, for only the freshly ground material is effective.   Hellebore has not survived the introduction of rotenone-containing insecticides, because of the lack of knowledge of the active constituents and of methods of standardization.

Of inorganic substitutes for the arsenicals **lead chromate** was suggested by Lefroy (77).   He claimed that this compound, if not as poisonous as Paris Green, was comparable to lead arsenate in insecticidal properties ; that, being yellow, it is more easily seen on the sprayed foliage ; that it is extremely insoluble ; that it does not decompose readily and that it is not easily washed off by rain. Tests by Johnson (78) with a lead chromate powder against Colorado Beetle gave unsatisfactory results as compared to the arsenicals. Moore and Campbell (79), who examined the insecticidal properties of a number of inorganic and organic derivatives, found **cuprous cyanide** as toxic as lead arsenate to Japanese Beetle and **cuprous thiocyanate** effective against the Tent Caterpillar *Malacosoma americana*, the latter product failing against Japanese Beetle.   The efficiency of cuprous cyanide as a stomach insecticide has since been confirmed by Bulger (80), Fleming and Baker (81) and Speyer (82).

Cuprous cyanide was included in Moore and Campbell's tests because it was thought that, by slow decomposition, hydrogen cyanide would be liberated as the active insecticide.   It was, however, shown that the compound is relatively stable when exposed on the leaf surface.   It would therefore seem of promise not only as a protective insecticide but as a fungicide (83).   When employed as a poison bait, admixed with bran or dried blood, Speyer found that decomposition of cuprous cyanide does occur with the result that the efficiency of the bait is lost.

An ingenious idea (U.S.P. 2062911) was that the insecticidal properties of chromium derivatives and of the thiocyanate group might be coupled in the co-ordination complex obtained by the fusion of ammonium dichromate and ammonium thiocyanate.   This

product, known as *Reinecke's Salt*, is ammonium diamminoch·romium tetrathiocyanate $(NH_4)[(NH_3)_2 Cr (SCN)_4]$ or, for convenience, ammonium reineckate. The insecticidal properties of this compound and of reineckates made by the substitution for the ammonium radical, of organic bases of known toxicity were examined by Guy (84) who found that the most potent of those tested was the piperidinium reineckate, which was as toxic to Mexican Bean Beetle (*Epilachna varivestis*) as an equal dose of lead arsenate, but had a greater speed of kill. Satisfactory tests were also made on Codling Moth larvæ and on Colorado Beetle but in field trials, in combination with protective fungicides, spray damage and a lower insecticidal efficiency were obtained, the result apparently of the decomposition of the reineckate in the presence of lime to form ammonium thiocyanate, a compound of intense phytocidal activity. The commercial development of these insecticides depends on the discovery of a satisfactory method for their stabilization.

Among the fifty compounds selected by McAllister and Van Leeuwen (85) as worthy of further trial as lead arsenate substitutes against Codling Moth was **triphenyl phosphine**. Guy (84) tested this compound and some of its phosphonium derivatives against Mexican Bean Beetle and Colorado Beetle and found both the **methyl triphenyl phosphonium chloride** and **iodide** approached lead arsenate in toxicity. The expense of manufacture and a tendency to injure foliage limit the insecticidal usefulness of these compounds.

Of organic compounds suggested as substitutes for the arsenicals, one of the oldest is **dinitro-*o*-cresol** (1-methyl-4 : 6-dinitrophenol) which was the active constitutuent of Antinnonin, a product introduced in 1892 (86) against the Nun Moth (*Lymantria monacha*). Hargreaves (87) found the ammonium derivative effective against larvae of *Pieris rapæ* L and *Spilosoma lubricipeda* Esp. Dinitro-*ortho*-cresol and its alkali salts were found to be powerful ovicides by Tattersfield, Gimingham and Morris (88) for which purpose they have now been commercially developed (see p. 223). Until derivatives of lower phytocidal properties (see 89, 90) are devised, it is unlikely that the dinitrocresols will find wide application as stomach insecticides for foliage use.

The success of certain organic sulphur compounds as fungicides led to a testing of a series of these products against mosquito larvæ (91). The most successful compound to be tested was

thiodiphenylamine (dibenzo-1 : 4-thiazine, phenothiazine). The potent insecticidal properties of this compound were established by contemporary investigators (see 84, 92) but trials of commercial thiodiphenylamine against Codling Moth gave results inferior to lead arsenate (93) due, probably to the high content of impurities *in the commercial product (94). Minor difficulties in the compounding of thiodiphenylamine for insecticidal use are difficult wetting and ready oxidation to dark-coloured compounds of inferior insecticidal properties and of objectionable appearance on sprayed fruit.* The addition of suitable antioxidants (e.g. B.P. 488428–9) retards oxidation, but attempts to find more stable derivatives of thiodiphenylamine have not been successful. Series of related compounds were examined by Guy (84) and by Schaffer, Haller and Fink (95), but none of equal toxicity was found. Indeed the substitution of the methyl group for the labile hydrogen atom attached to the nitrogen halved the toxicity to mosquito larvæ. Another disadvantage mentioned by Guy is a tendency of thiodiphenylamine to cause skin irritation.

An unusual compound, S_4N_4, known by the misleading name of **sulphur nitride,** was reported by Fulton (96) to be a stomach poison (U.S.P. 2101645). The chemistry and probable constitution of the compound are discussed by Arnold, Hugill and Hutson (97) and a probable disadvantage is its explosive character, not conspicuous in the pure product, but which may appear in the compounded products.

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INSECTICIDES (*continued*)—CONTACT INSECTICIDES

NICOTINE

The value of tobacco, a plant introduced into Europe about 1560,* as an insecticide was apparently known to Peter Collinson, who in 1746 wrote from England advising Bartram, an American botanist, to use water in which tobacco leaves had been soaked against the plum curculio (1). Scientific investigation traced the poisonous property of tobacco to the presence of nicotine, an alkaloid discovered as far back as 1828 by Posselt and Reimann. The separation of nicotine from waste tobacco provides one of the most valuable and well-standardized insecticides at present available.

The chemistry of nicotine is known with comparative thoroughness. The pure alkaloid is a mobile, colourless liquid boiling at 247° C., which on ageing takes on a brownish colour, deepening until almost black and becoming more viscous. It is soluble in water and possesses a disagreeable smell. Appreciably volatile, it may be distilled in steam, a property to which no doubt its early isolation was due.

Nicotine is a well-defined base forming soluble salts with organic and mineral acids. In the tobacco plant it is combined with malic and citric acids. It appears on the market both in the free state and as the sulphate, obtained by a patented process and sold under the name " Black Leaf 40," containing 40 per cent. of the base.

Both commercial nicotine and the sulphate keep well, apart from the " ageing " changes already mentioned. These changes do not appear, however, to be accompanied by any decline of the toxic properties of the materials. Upon exposure nicotine, being hygroscopic, absorbs moisture. According to McDonnell and Young (2) equilibrium is reached at a content of approximately 89 per cent. of nicotine, whereas with the sulphate equilibrium is established, by evaporation, at a content of about 45 per cent. nicotine.

* It is reported that in 1560 John Nicot sent seeds to the French king, describing them as germs of a medicinal plant of great value.

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Action on the Insect. McIndoo (3) from numerous trials concluded that nicotine acts, whatever be the manner of application, as a fumigant. The active agent appears to be nicotine vapour, which passes into the tracheæ of the insect and paralyses the nervous system. This same paralysis has been observed in the poisoning of higher animals by nicotine when it is considered that death results from asphyxia due to paralysis of the respiratory centre. With insects, however, the tracheæ and tissue contain sufficient oxygen to support life for several hours, whereas nicotine can prove toxic within a few minutes. De Ong (4) established a close parallel between the volatility of nicotine and its toxic action ; the salts of nicotine are much less volatile and are correspondingly less toxic than pure nicotine.

The possibility that the greater volatility of nicotine is not the only factor responsible for the greater toxicity as compared to that of its salts is suggested by Richardson and Shepard (5), who showed that, in solution, the free base is five to seven times as toxic as nicotine sulphate or hydrochloride to mosquito larvæ. As the acidity of the solutions was adjusted to ensure dissociation of the nicotine salts, this result indicates that the undissociated nicotine molecule is more toxic than the nicotine ion.

The need for a substitute for lead arsenate in Codling Moth control to lessen the difficulties of spray residue removal has prompted much research on the use of nicotine as a stomach poison. In this case volatility is a disadvantage and attention has been given to methods of " fixing " nicotine to reduce the rapidity of loss of toxicity by violatilization. Of the fixed nicotines, the tannate was found of promise by Headlee, Ginsburg and Filmer (6). Combinations of nicotine and bentonite have also become popular since their introduction by Driggers and Pepper (7), while a variety of other nicotine compounds and adsorption complexes have appeared in the patent literature, e.g. nicotine-peat (U.S.P. 2107058) (8), Quebracho-fixed nicotine (U.S.P. 2152236).

The ability of nicotine to function as an ovicide against Codling Moth was reported by De Sellem in 1916 (9) and Feytaud (10) observed that eggs of *Polychrosis botrana* failed to hatch after nicotine treatment in spite of the complete development of the

embryo. A similar " aborting " action of nicotine has been reported on Apple Sawfly, *Hoplocampa testudinea* Klug. (11), and was examined in detail by Shaw and Steer (12) and by Misaka (13). Possible explanations are the fixation of the nicotine by the egg-shell and surrounding plant tissue, the insect being killed by a stomach poison action at emergence, and the penetration of the nicotine to the embryo which is killed only when the development of the nervous system. is sufficiently advanced. The phenomenon is of practical value for it reduces the difficulty of correct timing of the application of nicotine sprays against pests such as Apple Sawfly.

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Action on the Plant. Although prior to the commercial production of nicotine and nicotine sulphate there may have been cases of spray injury due to tobacco extracts, no record can be found of any damage caused by nicotine itself in the use of nicotine washes and dusts. It would appear that in this respect nicotine, like many of the plant products used as insecticides, approaches the ideal.

Supplements for use in Nicotine Sprays. An intimate contact between spray and insect is an obvious requisite for a contact insecticide and if, as McIndoo (14) reported, nicotine acts in the vapour phase by penetration into the insect tracheæ, the addition of supplements to aid penetration should enhance its efficiency. Moore and Graham (15) examined the ability of liquids to enter the tracheæ of insects and found that of the aqueous solutions tested only soap solutions were capable of this penetration. O'Kane and his co-workers (16) and Wilcoxon and Hartzell (17) also

demonstrated the penetration of soap solutions, the latter showing that penetration occurred with live but not with dead larvæ of *Phlegethontius quinquemaculata* and suggesting that factors other than capillary forces are involved in penetration.

Of the penetratants suggested for use, soap has been recommended in a most emphatic manner. Moore (18) stated that the efficiency of free nicotine is sometimes increased 50 per cent. by the addition of soap. Its special virtue appears to lie in the fact that soap is a most efficient spreader and that, being alkaline in reaction, it does not affect the volatility of the nicotine. Further, soap itself has a definite insecticidal action, a point discussed later.

There have been placed on the market a number of soap preparations containing nicotine ready for use, but it was found that such products deteriorated more or less rapidly with an apparent loss of nicotine. This deterioration was investigated by McDonnell and Nealon (19), who showed that the loss of nicotine is due, not to volatilization but to the formation of an insoluble resinous product with which the nicotine is carried down. McDonnell and Graham (20) found that this insoluble condensation product was formed by oxidation and occurred only in preparations made from drying oils (i.e., unsaturated glyceride oils). When packed so that air was excluded, the preparations suffered no loss in nicotine content during two years of storage.

Soaps are, as we have already seen, compounds of fatty acids and alkalis. The suggestion has been made of employing nicotine itself as the base instead of the alkali, giving nicotine " soaps." Moore (21), for example, recommended the soap-like salt prepared by the combination of nicotine and commercial oleic acid. A number of nicotine " soaps " were examined by Hoyt (22), who found marked differences according to the type of fatty acid employed. Such compounds do not appear, however, to have found practical utilization. An idea of a similar character is the attachment of long side chains in a manner such that the nicotine molecule is made capillary active (B.P. 401,707). Austin, Jary and Martin (23) recorded preliminary trials of Tinocine D, a long-chain nicotinium bromide of this type, which indicated that insecticidal properties were not markedly reduced by this drastic change of the molecular structure of nicotine. Swingle and Cooper (24), however, found dimethyl nicotinium sulphate relatively ineffective in their trials.

The excellent penetrating properties of oils would seem to render

them particularly effective as nicotine supplements. It has been claimed, for example, that " Penetrol " functions as an activator for nicotine (25). The presence of free oil in this product was demonstrated by Martin (26) and it is not impossible that the high efficiency of the nicotine-Penetrol combination is associated with the penetrating properties of the oil present.

There is evidence that when employed as a stomach poison or ovicide, the addition of penetrants may be disadvantageous. Driggers and Pepper (27), for instance, referred to a proprietary product " Black Leaf 155 " which proved ineffective, as it contained too much spreader, causing a heavy run-off. Their contention was supported by analytical data and, for improving spray retention, they found that bentonite was of promise as a nicotine spray supplement.

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Nicotine Dusts. Dusts, prepared by the adsorption of nicotine or nicotine sulphate upon a finely divided " carrier " were first used experimentally by Smith (28) in 1917. As the efficiency of the dust would appear to depend, within limits, upon the rate of volatilization of the nicotine, their success may be connected with the relatively large surface area of the particles, upon which the nicotine is exposed to evaporation. Headlee and Rudolfs (29) have shown that for the nicotine dusts this volatilization is controlled more by the absorptive character of the carrier and that the more finely divided " colloidal " carriers are inferior to the crystalline carriers. This conclusion was confirmed by Thatcher and Streeter (30), who classed

the " colloidal " kaolin, kieselguhr and talc as " absorbent " carriers, the crystalline gypsum, sulphur, etc., as " inert " carriers. It is supposed that the nicotine adsorbed by the more finely divided carrier is less freely volatilized.

With the nicotine sulphate dusts, the chemical factor of the liberation of the nicotine comes into play. Headlee and Rudolfs recommended for use as the carrier a mixture of dolomite (magnesium and calcium carbonates) and hydrated lime, both of which will react with the nicotine sulphate. Thatcher and Streeter classed such carriers, called by Headlee and Rudolfs " chemical accelerators," as " active," recommending the use of hydrated lime or precipitated chalk.

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Compounds of Structure akin to Nicotine.

The unique insecticidal power of nicotine among the alkaloids has provoked much study as other alkaloids equally toxic to higher animals are relatively innocuous to insects. It has been thought that the toxicity may be related to its molecular structure and that compounds of similar structure might possess similar insecticidal properties. The point has an important practical application for, as no satisfactory commercial synthesis of nicotine is yet available, a synthetic substitute would be of great value.

The chemical constitution of nicotine was established by its successful synthesis in 1904 by Pictet and Rotschy (31), as 3-(1-methyl-2-pyrrolidyl) pyridine, represented on p. 307. The nicotine molecule contains two nuclei, pyridine and pyrrolidine, the hydrogenated derivative of pyrrol. Pyridine and pyrrol have been shown to be but feebly toxic to insects (32). In testing the insecticidal properties of a number of compounds possessing a structure akin to that of nicotine, Richardson and Smith (33) observed the high toxicity of a crude dipyridyl oil. The dipyridyls are compounds of two pyridine molecules linked by the elimination of one atom of hydrogen from each molecule. In this way six isomers are possible, all of which were present in the dipyridyl oil which these

workers prepared. The crude oil was found to possess insecticidal properties greater than any of the dipyridyls. This high toxicity was eventually traced to the presence of 3-(2-piperidyl)pyridine, a compound of structure represented on p. 308, and of toxicity to *Aphis rumicis* equal to that of nicotine (34). This compound has been named **Neonicotine.**

The same compound has now become available as a naturally occurring plant product present in *Anabasis aphylla* L. (Chenopodiaceæ), a weed common in Turkestan. Orékhov and Menschikov (35) isolated some 2 per cent. of alkaloids from this plant, the mixture yielding, in greatest measure, a liquid alkaloid to which they gave the name **Anabasine.** They proved this compound to have the structure 3-(2-piperidyl)-pyridine and, in view of its relationship to nicotine, the alkaloids were extracted on a commercial scale. The identity of anabasine and neonicotine, apart from the fact that the former is lævorotatory, was confirmed by Smith (36). The insecticidal properties of anabasine (37, 38) were critically examined by Richardson, Craig and Hansberry (39) but the relationships between structure and toxicity shown in the nicotine series are discussed in greater detail on pp. 306–308.

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PYRETHRUM

The early history of the use of pyrethrum for insecticidal purposes is obscure. According to Lodeman (1), an Armenian named Jumtikoff discovered that an effective insect powder used by the tribes of the Caucasus was prepared from the flower-heads of a certain species of pyrethrum. His son, in 1828, began the manufacture of the powder on a large scale and, in 1850, the product was introduced into France. Gnadinger (2) has stated that the earliest

sources were the species *Pyrethrum roseum* Bieb. and *P. carneum* Bieb. and that the more effective *P. cinerariæfolium* Trev. was later discovered in Dalmatia about 1840.

Pyrethrum is to-day derived mainly from these three species, which have been recognized by the United States Department of Agriculture as the only species suitable for the manufacture of insecticides. Other species of *Pyrethrum* reputed to be toxic to insects are listed by Gnadinger. The so-called African or German pyrethrum, at one time used in pharmacy under the names " *Radix pyrethri* " and " Pellitory root," is derived from the roots of *Anacyclus pyrethrum* D.C. and *A. officinarum* Hayne, and finds no use in horticulture. To avoid confusion the active principles of pellitory root, which were originally named " pyrethrin," have been re-named " pellitorine " (3).

Pyrethrum was slow to gain popularity as an insecticide, for erratic results were obtained which are now known to be associated with the ready loss of its toxic properties on exposure and the lack of suitable methods for its standardization. The publication, in 1924, of the work of Staudinger and Ruzicka on the identification of the active constituents and the need for an insecticide non-poisonous to man and warm-blooded animals, has led to efforts to extend the use of pyrethrum in horticulture (4). The most successful application of pyrethrum has been in the development of household insecticides and in the United States, in 1928, the importation of pyrethrum amounted to 13,689,000 lb. (2).

Knowledge of the nature of the active constituents of *P. cinerariæfolium* is due largely to the classical researches of Staudinger and Ruzicka (5), but, of earlier work, that of Fujitani (6) and Yamamoto (7) is noteworthy. Fujitani isolated an effective constituent " Pyrethrone " which he showed to be a mixture of esters, the compounds of an alcohol " Pyrethrol," with various acids, of which two were later isolated by Yamamoto.

Pyrethrone was critically examined by Staudinger and Ruzicka, who isolated two esters to which they gave the names Pyrethrin I and Pyrethrin II. These were proved to be the compounds of a ketonic alcohol " Pyrethrolone " with two acids which were shown to be (I), a monocarboxylic acid which was ultimately proved by synthesis to have the structure :

$$C(CH_3)_2:CH.CH \underset{\diagdown CH.COOH}{\overset{\diagup C(CH_3)_2}{\diagup}}$$
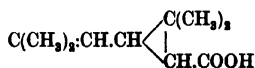
and (II), a closely-related dicarboxylic acid :

$$\text{COOH.C(CH}_3\text{):CH.CH}\underset{\text{CH.COOH}}{\overset{\text{C(CH}_3)_2}{\diagdown}}$$
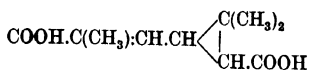
The alcohol, pyrethrolone, on reduction gave tetrahydropyrethrone which was considered, by Staudinger and Ruzicka, to be 3-methyl-2-*n*-amyl-*cyclo*-pentanone. In repeating this work, La Forge and Haller (8) obtained evidence that the empirical formula of pyrethrolone contained two hydrogen atoms less than that deduced by Staudinger and Ruzicka and that it is a *cyclo*-pentanolone derivative. La Forge and Haller (9) also examined the —C_5H_7 side chain of pyrethrolone which Staudinger and Ruzicka suggested contained the allene system —CH:C:CH—, an unusual system to find in natural products. As their results gave no indication of the more usual conjugated system —CH:CH—CH:CH—, they regarded Staudinger and Ruzicka's opinion as the more probable. Pyrethrolone may therefore be given the structure :

$$\begin{array}{c} \text{CH}_2\text{—C.CH}_3 \\ | \qquad \diagdown \\ \text{HO.CH—CO} \end{array}\!\!\!\!\text{C.CH}_2\text{.CH:C:CH.CH}_3$$
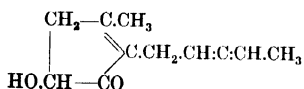
Pyrethrolone and the two acids themselves were found, by Staudinger and Ruzicka, to have but slight insecticidal properties, but the ester regenerated from the monocarboxylic acid was as insecticidal as the natural product. The ester from pyrethrolone and the dicarboxylic acid showed a low insecticidal activity but pyrethrolone esterified with the dicarboxylic monomethyl ester was highly toxic. The two pyrethrins may therefore be given the following structures :

$$\begin{array}{c}
\text{CH}_3 \\
| \\
\text{C} \\
\diagup\diagdown \\
\text{H}_2\text{C} \qquad \text{C.CH}_2\text{.CH:C:CH.CH}_3 \\
| \qquad\quad | \\
\text{O—HC———C —O} \\
| \\
\text{CO} \\
| \\
\text{CH} \qquad \text{✱} \\
\diagup\diagdown \\
\text{(CH}_3)_2\text{C—CH.CH:C(CH}_3)_2
\end{array}$$

<div align="center">Pyrethrin I</div>

$$CH_3$$
$$|$$
$$C$$

$$H_3C \quad C.CH_2.CH:C:CH.CH_3$$
$$| \qquad |$$
$$O—HC——C{=}O$$
$$|$$
$$CO$$
$$|$$
$$CH$$

$$(CH_3)_2C—CH.CH:C \Big\langle {}^{COOCH_3}_{CH_3}$$
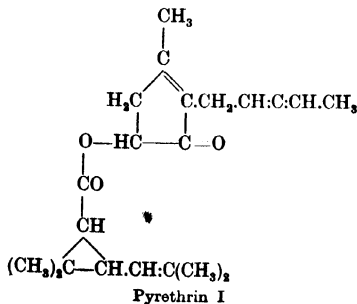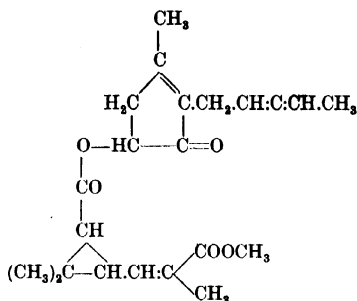
Pyrethrin II

Difficulties in the analytical standardization of pyrethrum raised the question of the relative toxicity of the two pyrethrins. Staudinger and Ruzicka concluded that, of the two pyrethrins regenerated by esterification, I was more toxic than II to cockroaches, a conclusion confirmed on *Aphis rumicis* by Tattersfield, Hobson and Gimingham (10) and by Wilcoxon and Hartzell (11), who separated the pyrethrins by physical methods. Gnadinger and Corl (12), however, found the two pyrethrins, separated by the fractional crystallization of their semicarbazones, of almost equal toxicity to House Flies (*Musca domestica* L.), a result not confirmed by Haller and Sullivan (13). These divergencies seem to be explained by the observation of Hartzell and Wilcoxon (14) that the relative toxicity of the two pyrethrins depends on the physical condition in which they are applied and by the conclusion of Sullivan, Haller, McGovran and Phillips (15) that the two pyrethrins differ in their physiological action. Hartzell and Wilcoxon found that pyrethrin I is more toxic than II to both *A. rumicis* and *M. domestica* when applied in aqueous dispersion but when dispersed in an emulsified oil-solution there was little or no differences in toxicity. Sullivan and his co-workers showed that pyrethrin II had a more rapid paralytic action (knockdown) but a lower insecticidal effect than pyrethrin I on *M. domestica*.

Staudinger and Ruzicka examined the insecticidal properties of a large number of esters prepared from pyrethrolone and various organic acids and from the monocarboxylic acid and various alcohols, but few proved toxic. The ester of 1-methyl-2-allyl-*cyclo*-pentanolone showed insecticidal powers but not of the same order as the pyrethrins. It is apparent that small changes in the structure of the pyrethrin molecule markedly affect its insecticidal properties (13).

Inspection of the structure of the pyrethrins reveals a high degree of unsaturation indicative of instability. A ready decomposition of the pyrethrins with the resultant loss of insecticidal properties is therefore to be expected. Staudinger and Harder (16), for example, pointed out that loss of toxicity might occur in " Savon-pyrèthre," an alcoholic-soap extract of pyrethrum popular on the Continent, firstly because hydrolysis of the pyrethrins would probably be accelerated by the presence of alkali, secondly because of the possible replacement of pyrethrolone by ethyl alcohol. Tattersfield and Hobson (17) found, however, that alcoholic extracts of pyrethrum retained their toxicity in temperate climates over many months, whilst, in alkaline dispersions, the loss of toxicity was surprisingly small.

It has for long been known that pyrethrum flowers lose their insecticidal potency on storage and Abbott (18) showed that, although the whole flower-heads could be kept, in sealed containers, for over five years without deterioration, the ground flower-heads in open dishes practically lost their toxicity within 150 weeks. Tattersfield and Hobson (17) also showed the loss of toxicity of ground flowers exposed to light and air in thin layers, and they observed a rapid loss of activity of exposed dusts prepared by the absorption of pyrethrum extracts upon absorbent carriers such as talc and kieselguhr. Tattersfield (19) showed that loss of activity was most rapid in dusts exposed to light and air, an indication that oxidation is an important factor in the inactivation of the pyrethrins. Tattersfield therefore investigated the effects of the addition of anti-oxidants and found that many phenolic derivatives such as pyrocatechol, resorcinol, hydroquinone, pyrogallol and tannic acid, but neither phenol nor phloroglucinol, conferred a large measure of protection against loss of toxicity. Tattersfield and Martin (20), in addition to confirming this conclusion, showed that the loss of toxicity ran parallel to the loss of pyrethrin I as determined by the acid method (21).

The effect of the pyrethrins upon the insect is of a startling rapidity and, in the case of M. domestica, Richardson (22) was able to employ the speed of paralytic action as a measure of toxicity of pyrethrum extracts. According to Chevalier and Mercier (23), the lower the animal the more rapid is the establishment of paralysis and the pyrethrins appear to be harmless to warm-blooded animals. The rapidity of the narcotic effect and the recovery of insects from sub-lethal doses is referred to by Tattersfield (24). From a histo-

pathological study of the nerves of insects killed by pyrethrum extract, Hartzell (25) concluded that death is caused by the destruction of the cells of the central nervous system. Swingle (26) demonstrated that pyrethrum extract is non-toxic when taken by the mouth and that it functions, in the true sense, as a contact insecticide.

The rapid paralytic action of the pyrethrins renders pyrethrum extracts of value for admixture with slower but more certain contact insecticides. Such combinations afford possibilities of synergistic action which has been studied in pyrethrin-rotenone mixtures by Le Pelley and Sullivan (27) and by Bliss (28). Apart from rotenone-containing substances, other insecticides employed in compounded pyrethrum insecticides include the organic thiocyanates (see p. 222), α-naphthyl*iso*thiocyanate (29) and *iso*butyl undecylenamide (30).

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ROTENONE AND RELATED INSECTICIDES

In 1848, Oxley (1) suggested tuba-root, used in the Malay Archipelago as a fish and arrow poison, for the control of the insect pests of the nutmeg. Hooker (2) recorded that tuba-root had been used by the Chinese in Singapore for the preparation of an insecticide. The main source of tuba-root is the root of *Derris* * *elliptica* (Wall.) Benth. and the best known of its active principles is rotenone.

Sources of Rotenone, etc. The success of tuba-root as an insecticide encouraged trials with other plants employed by natives in various parts of the world as fish poisons. The most successful have been plants of *Derris*, *Lonchocarpus* and *Tephrosia* (*Cracca*) spp., further particulars of which are given below. A review of the insecticidal properties of many plants reputed to possess fish-poisoning properties was made by Tattersfield and Gimingham (4), who reported favourably upon *Mundulea suberosa* Benth., from India, and *Neorautanenia* (*Rhynchosia*) *fisifolia* (Benth.) C. A. Sm. from S. Africa. It is of interest to note that all the fish-poison plants having insecticidal properties are of the Leguminosæ.

Derris spp. The botanical indentification of the species of Derris employed in early work was made difficult by the erratic flowering habits of the plant and by the diversity of habits within the species. The sources of derris root in the Malay Peninsula have been described by Henderson (5), the most important commercially being *D. elliptica* and *D. malaccensis* Brain. Both species contain varieties, six of the former species being classified by Henderson. The latter species, when grown under cultivated conditions, acquires habits different from the wild variety and is distinguished by the name *D. malaccensis* var. *sarawakensis* Hend. Cahn and Boam (6) found it necessary to differentiate, for chemical reasons, a Sumatra type of derris resin which they considered was probably derived from the roots of the latter variety.

Lonchocarpus spp. The fish-poison plants of S. America are

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* The name *Derris* Lour, is antedated by *Deguelia* Aubl. (3) but, in view of the widespread use of the former, it has been retained.

known collectively as " barbasco " in the Spanish-speaking countries, as " cubé " in Peru, and generally as " Timbo." They were mentioned by Geoffrey in 1892 (7) and have since been commercially developed. The most important of the Peruvian species was, in 1930 (8), identified with *L. nicou* (Aubl.) D. C. but has now been given separate status, *L. utilis*, sp. n., by Krukoff and Smith (9). These investigators stated that the principal species in Brazil is *L. urucu*, other species of interest being *L. martynii* and *L. chrysophyllus*, which are probably the White Haiari and Black Haiari respectively examined by Tattersfield, Gimingham and Morris (10).

Tephrosia spp. The insecticidal properties of *T. Vogelii* Hook. were investigated by Tattersfield, Gimingham and Morris (11), toxic principles being found in the leaves and seed. The following year (10), they showed that the roots of *T. toxicaria* Pers. possessed insecticidal principles. In later work, Tattersfield and Gimingham (4) found the roots and stem of *T. macropoda* Harv. of insecticidal value. The possibilities of the commercial development of *T. Vogelii*, which is indigenous to East Africa, are being explored by Worsley (12). The predominant insecticidal constituent of these species appears to be tephrosin, but a small content of rotenone has been found in *T. virginiana* L., which is of particular interest as it is a weed, Devil's Shoestring, common in southern U.S.A. (13).

The distribution of rotenone and allied compounds in other species of Papilionaceæ has been examined by Worsley (14) who has tabulated their occurrence on a histological basis.

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The Chemistry of Rotenone and related Compounds.
Extraction of derris or lonchocarpus root with organic solvents
yields a resin from which, in ether or carbon tetrachloride, a white
crystalline compound is obtained. That from lonchocarpus was
called nicouline by Geoffrey (15) in 1895. In 1911 Lenz (16), who
isolated this compound from *D. elliptica*, gave it the name Derrin
and to it attributed the fish-poisoning properties of derris root.
Independently, Ishikawa (17) in 1917 obtained a similar crystalline
material from tuba-root and named it tubatoxin. Tubatoxin was,
in 1923, shown by Kariyone and his colleagues (18) to be identical
with a product first isolated, in 1902, by Nagai (19) from " Roh-
ten," * which he named rotenone. The latter name has now
been generally accepted for this compound, which forms colourless
crystals of m.p. 163° C.

The molecular structure of rotenone was deduced almost simul-
taneously by La Forge, Haller and their colleagues in the United
States (21), by Robertson (22) in this country, by Takei and his
colleagues (23) in Japan and by Butenandt and co-workers (24)
in Germany. It is represented on p. 190 as formula I.

From the resin remaining after crystallization of the rotenone
from extracts of derris and related plants, a number of other com-
pounds have been isolated. Toxicarol, first isolated by Clark (25),
was shown by George and Robertson (26) to be 15-hydroxy-
deguelin. Deguelin, also first isolated by Clark (27), was found to
be isomeric with rotenone and was assigned the formula III on
p. 191 by Clark (28) and by Robertson (22). An alternative
formula suggested by Heyes and Robertson (29) is now known as
β-deguelin but, from the work of George and Robertson, it appears
that this compound and the related β-toxicarol are not present in
the plant.

With deguelin, Clark (30) also isolated tephrosin, a compound
named by Hanriot (31) who had, in 1907, obtained it from the
leaves of *T. Vogelii* as white crystals of m.p. 187° C. Hanriot
showed that it was accompanied by an oily liquid which he called
tephrosal. Hanriot's results were confirmed (32) by Tattersfield,
Gimingham and Morris (33), but Clark considered Hanriot's te-
phrosin to be a mixture of deguelin and another substance of m.p.
197–198° C., a separation which Worsley (34) was unable to repeat.
Clark adduced evidence that the substance of m.p. 197–198° C.,

* " Roh-ten " has been identified as *D. chinensis* Benth. or *Millettia
taiwaniana* Hayata (20).

to which he applied the name tephrosin, is a hydroxy-deguelin, the hydroxy-group replacing the hydrogen atom at either carbon 7 or carbon 8 (Formula I, below).

Deguelin, toxicarol and tephrosin are optically inactive and doubt was expressed by Clark of their occurrence in the original plant material. It is probable that they are formed, by chemical change during the process of extraction, from precursors in the roots. The intricate changes of enolization, racemization and isomerization, which rotenone and allied compounds undergo on alkaline treatment of the type used by Clark, have been discussed by Cahn, Phipers and Boam (35). The search for the precursors of these compounds has led to the isolation of other compounds, e.g. sumatrol by Cahn and Boam (36), shown by Robertson and Rusby (37) to be 15-hydroxyrotenone, thus bearing the same relationship to rotenone as toxicarol does to deguelin. Tattersfield and Martin (38) isolated, from *D. malaccensis*, *l*-α-toxicarol, which is probably the form in which toxicarol exists in the resin. Harper (39) has recently established that the precursor of an optically-inactive compound first isolated by Buckley (40) is *l*-elliptone (Formula IV, p. 191), a derivative of *iso*rotenone but without the *iso*propyl side chain —CH.(CH₃)₂. This compound and the corresponding 15-hydroxy-derivative were also isolated by Meyer and Koolhaas (41).

The structures of rotenone and the known allied compounds have, therefore, much in common. All can be regarded as built up of a four-ring chromenochromanone structure (rings A, B, C, D) by the addition of a fifth ring (ring E) which is of type I in rotenone and sumatrol, of type II in *iso*rotenone and elliptone, and of type III in deguelin, tephrosin and toxicarol.

I
Rotenone
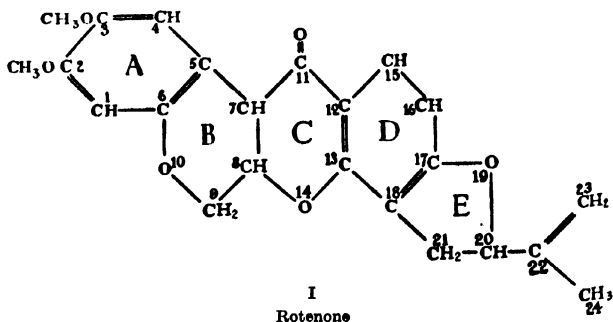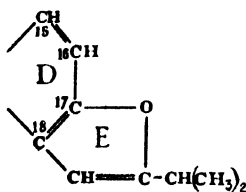
II
Isorotenone
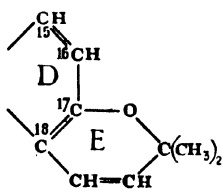
III
Deguelin
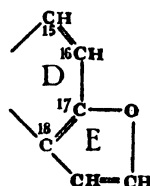
IV
Elliptone
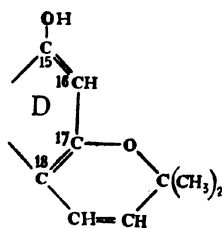
V
α-Toxicarol
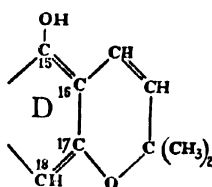
VI
β-Toxicarol

Cahn, Phipers and Boam (42) have been able to account for over 80 per cent. of typical derris resins in terms of these compounds. *D. elliptica* resin consists of about 40 per cent. of rotenone and 27 per cent of *l*-deguelin, the content of sumatrol and of *l*-toxicarol being low. Resins of *D. malaccensis* of the Sumatra type, on the other hand, contain 50–60 per cent. of *l*-toxicarol, 12 per cent. *l*-deguelin, 5–15 per cent. sumatrol and but 2–5 per cent. rotenone. In plants of *T. dephrosia* spp., with the exception of *T. virginiana*, tephrosin has been the predominant compound isolated.

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The Evaluation of Sources of Rotenone, etc. The isolation of rotenone and other compounds from derris and lonchocarpus roots was followed by the examination of their insecticidal properties in the hope that, on the basis of this knowledge and of analytical methods for the estimation of the content of these compounds in the roots, a chemical evaluation of the latter would become possible. An early suggestion, by Tattersfield and Roach (43), for the evaluation of derris root was by the estimation of the ether extract and the confirmation of the genuineness of the extract by the determination of methoxy ($-OCH_3$) content. Following the recognition of the high insecticidal potency of rotenone, the estimation of this constituent by crystallization from the ether (44) or carbon tetrachloride (45) extract was suggested and widely used. It was, however, found that derris extracts poor in rotenone as estimated by these methods were highly insecticidal (46), that derris extracts after removal of the crystallizable rotenone were highly piscicidal (47) and that derris extracts were more toxic to mosquito larvæ than indicated by the amount of rotenone obtained from them (48).

A possible explanation of the failure of these crystallization methods to evaluate insecticidal properties arose through the observation of Takei *et al.* (47) of the presence of further amounts of rotenone in derris extracts from which rotenone had been crystallized from ether solution. Cahn and Boam (49) also recovered " hidden rotenone " from solutions of a Sumatra-type resin which yielded no rotenone from carbon-tetrachloride solution. Many methods, differing in solvents and in methods of extraction, have

been proposed (see 50) involving a prior removal of toxicarol or the addition of rotenone to increase the concentration to a point overcoming the inhibitory effect of the resinous constituents on crystallization.   Alternatively colorimetric methods based on the Gross and Smith (51) or the Goodhue (52) tests, to which both rotenone and deguelin respond, optical methods such as used by Worsley (53) and chemical methods involving the determination of the " dehydro " derivatives devised by Takei *et al.* (47) and modified by Tattersfield and Martin (54) have been tried.

Though satisfactory correlations between toxicity as evaluated by these methods and as determined by biological assay have been recorded for a limited number of related plant materials, the general finding is that, when applied to a wider range, these methods have proved inadequate (55).   It is possible that the failure to trace general correlations is due to difficulties in the methods of biological testing.   The compounds and extracts tested, being insoluble in water, are usually applied in the form of suspensions made by adding a solution of the substance in an organic solvent to an aqueous solution.   The influence, on toxicity, of physical factors such as degree of fineness or of dispersion has already been mentioned (see p. 110), and there is little doubt that the insecticidal properties of these suspensions will likewise depend to some extent on their degree of dispersion.   Indeed, Cahn, Phipers and Boam (56), in stressing the importance of this factor in the biological evaluation of derris, recorded that suspensions of rotenone had proved ineffective in the Craufurd-Benson (57) test on *Ahasversus advena* though the addition of rotenone to derris extract increased its toxicity.   The rotenone suspension failed, it was suggested, because the active constituent was presented to the insect in large crystalline aggregates whereas, in the presence of the extract, it was dispersed in finely-divided amorphous particles.

Two points require comment.   The observations that the insecticidal properties of a derris resin are greater than would be expected from the rotenone content may be explained by the dispersing properties of the resin and need not be wholly due to the presence of components other than rotenone of direct insecticidal properties. Secondly, comparisons of the insecticidal activity of rotenone and allied compounds or of the resins of different species or varieties of plant may lead to erroneous conclusions unless the physical factors are rigidly controlled.   It seems therefore unwise to discuss the relative insecticidal potencies of rotenone and the related

products except to mention that, in most comparisons yet made, rotenone has proved the most toxic. Tattersfield and Martin (58), from the results of carefully standardized tests on *Aphis rumicis* of suspensions made by the addition of alcoholic solutions to dilute saponin solutions, gave the order of toxicity as :

Rotenone > *D. elliptica* resin > Sumatra-type resin > Sumatrol = *l*-α-toxicarol > inactive toxicarol.

In view of the high insecticidal properties of rotenone and the value of the resins as dispersing agents or as insecticides, a convenient evaluation of derris and lonchocarpus roots may be based on their content of rotenone and of total ether extractives, a method which has survived in commercial practice.

In the case of plants such as *T. Vogelii*, in which rotenone is not the predominant insecticide, the estimation of rotenone content will not be suitable for their analytical standardization. Worsley (59) traced a rough correlation between the toxicity, to citrus aphides, of extracts of various parts of the plant (*T. Vogelii*) and their content of crude tephrosin, though the pods exhibited a toxicity augmented by the presence of tephrosal. As, however, he was unable to confirm the observation of Tattersfield, Gimingham and Morris (60), that the resinous constituents of *T. Vogelii* have a greater toxicity than the crystalline products, a definite conclusion upon the chemical evaluation of extracts of *T. Vogelii* would be premature.

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The Utilization of the Insecticidal Properties of Rotenone, etc. Up to the present the usual method of applying rotenone and the related insecticides to plants has been in the form of the finely-ground root, either as a suspension or, admixed with a suitable carrier, as a dust. Although it is not suggested that such methods are ineffective, indeed there are reports (e.g. 61) that the ground derris root is superior to derris extracts, yet this procedure has the disadvantages that transport charges are disproportionately high because of the bulkiness and high content of inert material, and that the finely-ground root is difficult to sample (62), for which reason it is usually packed in small lots for grower's use. There is therefore a need for suitable methods for the preparation of concentrated extracts of derris and related plants. Worsley (63) referred to this requirement in the use of *T. Vogelii* as a substitute for nicotine in East Africa and investigated methods suitable for the extraction of crude tephrosin and for the preparation of concentrates which, by admixture with water or other simple process, furnish the required spray.

Much of the work on this problem has dealt with the employment of rotenone itself because of the ease with which it can be isolated from derris and lonchocarpus extracts. In view, however, of the residual toxicity of the resin after the removal of the crystalline rotenone, it would seem more economical to employ the total resin for the preparation of concentrates. Conclusions reached upon the stability of rotenone are probably applicable to rotenone-containing resins.

As rotenone is relatively insoluble in water and hydrocarbon oils, its use in sprays requires the employment of rotenone solvents, the reactions of a number of which have been examined by Davidson and Jones (64). They observed that in certain solvents, such as pyridine, the rotenone is decomposed with the formation of products of low insecticidal properties. The yellow colour of the decomposition products recalled the earlier observation of Tattersfield and Roach (65) that such products were formed when alcoholic solutions of rotenone were exposed to light. This decomposition is of important practical significance, particularly when rotenone is employed as a protective insecticide, for the toxicity of the spray deposit exposed to air and light upon the leaf surface should be

as permanent as possible.   Jones and Haller (66) showed that the yellow decomposition products are dehydrorotenone and rotenonone. Dehydrorotenone is derived from rotenone by the elimination of the hydrogen atoms at carbons 7 and 8 of formula I (p. 190) to form a double bond.   The further oxidation to rotenonone involves the replacement of the two hydrogen atoms at carbon 9 by oxygen. Oxidation readily occurs in alkaline solution but it has been shown that dihydrorotenone is more resistant to oxidation than rotenone. Dihydrorotenone is readily formed by the catalytic hydrogenation of rotenone (U.S.P. 1945312) which reduces the double bond of the *iso*propenyl side chain ($-C(CH_3):CH_2$) at carbon 20 to the *iso*propyl group ($-CH(CH_3)_2$).   Dihydrorotenone has been proved an effective stomach poison (67) and it has been suggested (68) that it might be superior to rotenone for this purpose because of its greater stability on exposure.   This suggestion has not apparently been adopted in practice.

The ready oxidation of rotenone in the presence of alkali and the resultant reduction of toxicity indicate that it is unwise to employ supplementary materials of an alkaline reaction with rotenone-containing sprays or dusts.   The use of soaps, for example, may increase this instability (see e.g. 69) whereas, for dusts, the use of carriers such as hydrated lime (see e.g. 70) is not recommended for the same reason.   When derris root or extract is used as a contact insecticide, the required wetting and penetration may be obtained by the addition of non-alkaline spreaders, in particular, the oils.   Kearns, Marsh and Martin (71) found a petroleum oil emulsion better than the water-soluble wetters tested and suggested that this superiority may be due, in part, to the solvent properties of the oils.   In view of the low solubility of derris resins in petroleum oils, the use of other oils and of intermediary solvents (see e.g. 72) is being explored.

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Action on the Insect. The mode of action of rotenone on the insect is unknown, but Hartzell (73) was unable to trace any action upon the nervous system. He recorded a suggestion that the respiration is involved, which is in accord with the general observation of the slowness with which the insect is affected and its rare recovery. Tischler (74) observed that the treated insects show severe respiratory disturbances, which he suggested was the primary physiological action of derris.

In addition to their high potency as contact insecticides and acaricides (75), rotenone and derris extracts are widely employed for the control of leaf-eating larvæ towards which the insecticide has been shown to function as a stomach poison (76). Miller (77), however, considered that his experiments indicated an action through the insect integument rather than through the intestine. A deterrent action is generally accepted but the remarkable observation of Fulton and Mason (78), that derris constituents are translocated from the surface of sprayed bean leaves to leaves developing after the application of the spray rendering them distasteful to *Epilachna varivestis* has not yet been confirmed.

A striking feature of rotenone and the related insecticides is their high degree of specificity. Although extremely toxic to insects and fish, they are relatively harmless to warm-blooded animals (79). Ambrose and Haag (80) concluded that the possibilities of acute poisoning by the ingestion of rotenone and related compounds were negligible though, when administered orally in olive oil, derris was appreciably toxic to rabbits and, according to Mathews and Lightbody (81), to rats. The danger of the inhalation of derris dusts, to which milling operatives are exposed, were stressed by Ambrose and Haag. There are indications that a degree of specificity is also shown among insects and the practice of assessing the insecticidal efficiency of derris preparations by their piscicidal properties must be regarded as dangerous. Ginsburg and Schmitt (82) have questioned the general reliability of comparisons of insecticidal efficiency based upon tests with insects of only one group.

It is early in the history of rotenone and the related compounds to speculate upon the reasons for the specific toxic properties which makes them such useful insecticides. It is of interest, however, to

note the suggestion of Priess (83), in 1911, that piscicidal properties are associated with the lactone group, of which an essential feature is a ring structure containing oxygen as a member of the ring. A striking feature of the rotenone molecule is the presence of oxygen-containing rings, in particular, the central pyrone ring and the terminal five-membered furan ring. Substitution of the latter by the six-membered pyran ring, as in deguelin, reduces toxicity, though the residual insecticidal properties are still high. Gersdorff (84), from an examination of the piscicidal properties of rotenone and seven related compounds, concluded that, in general, the dihydro derivatives, formed by the saturation of the *iso*propenyl group, are more toxic than the parent compound, that. the substitution of one of the hydrogen atoms 7 or 8 in formula I (p. 190) or in dihydro-rotenone by the acetate (–O.CO.CH₃) or hydroxyl (–OH) groups reduces the toxicity of the parent compound. That these particular hydrogen atoms are of importance in determining toxicity is also shown by the lower activity of dehydrorotenone, in which the possibility of enolization between carbons 7 and 11 is eliminated.

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THE HYDROCARBON OILS

As implied by their name, the hydrocarbon oils comprise those oils of which the predominant constituents are compounds solely of hydrogen and carbon. They have usually been classified into petroleum (mineral) oils, a group subdivided by reference to origin, e.g. Pennsylvanian, Mexican, and into tar oils described by the source of the tar, whether high-temperature carbonization, coke oven, etc., from which the oil was distilled.

Sufficient is now known, however, of the properties of the hydrocarbon oils as spray materials to justify a physico-chemical classification. Chemically, the hydrocarbon oils are mixtures of a complexity which defies separation to individual compounds, but a chemical basis for classification is made possible by the observation that the compounds present fall into a limited number of groups. Within each group are compounds of similar molecular structure but differing in the number of carbon atoms present in the molecule and forming a series in which each member contains one —CH_2— group more than its lower neighbour. In such homologous series, the individual hydrocarbons are of similar chemical properties, but the different groups can be differentiated, by chemical methods, into the following three classes :

(1) The *saturated hydrocarbons*, which, by reason of their chemical inertness, remain unchanged when the oil is treated with reagents such as sulphuric acid. The other groups of hydrocarbons are, by this process, sulphonated to acid-soluble derivatives or are polymerized to a sludge leaving the saturated oils as an unsulphonated residue. This reaction, which is the basis of the oldest method of refining petroleum oils, when carried out under standard conditions, is used for the determination of unsulphonated residue, a figure which gives a measure of the degree of refinement of a particular oil.

(2) The *unsaturated hydrocarbons* which, containing unsaturated linkages (i.e. carbon atoms united by two or more valency bonds), react with reagents such as iodine which enter the molecule at the double bond. If this reaction is carried out under standard conditions, an iodine value is obtained which gives a measure of the relative number of unsaturated linkages in the molecular structure of the compounds present in the oil.

(3) The *aromatic hydrocarbons* which are a special group of unsaturated hydrocarbons having the aromatic properties associated with the conjugated double bonds of the benzene nucleus. Hydrocarbons of this group are distinguished by certain tests of which one of the simplest utilizes the solubility of such compounds in dimethyl sulphate, a reagent in which high-boiling oils of the first and second groups are insoluble. The percentage of neutral oil soluble in dimethyl sulphate thus affords a measure of the content of aromatic hydrocarbons.

This chemical classification, which is the simplest necessary for the explanation of the properties of the hydrocarbon oils as spray materials, is supplemented by a physical classification which serves

to characterize not so much the type of compound present as the mean molecular weight of the mixture of hydrocarbons constituting the oil. In such homologous series the boiling-point of the hydrocarbon increases as the series is ascended. Distillation, which is the first process to which crude oils and tars are subjected, results in a fractionation according to molecular weight. The boiling range of the oil is therefore an important item in the description or specification of a particular oil though, in the case of petroleum oils, it has been found possible to substitute, for this criterion, the viscosity of the oil. In general, the greater its molecular weight, the more viscous the hydrocarbon. Like viscosity, the specific gravity of the oil is closely correlated with and increases with boiling range, but the correlation is affected by the relative proportions of the homologous groups of which the oil is made up. As a general rule, with oils of similar boiling range, the higher the specific gravity the greater the proportion of unsaturated and, in particular, the aromatic hydrocarbons present.

Reviewing the status, under this physico-chemical classification, of the older definitions employed to characterize hydrocarbon oils, the petroleum oils consist mainly of hydrocarbons of the saturated and unsaturated groups. Petroleum oils from certain oil fields, e.g. Borneo, are especially rich in aromatic hydrocarbons and the crude oils may contain constituents such as the naphthenic acids (see p. 86), sulphur compounds and nitrogenous derivatives. Distillation yields fractions, the more important of which for insecticidal purposes are the kerosene and lubricating oils. The kerosenes are those oils of boiling range between approximately 150° and 300° C. more familiar in this country as the paraffin employed as a burning oil. Fractions of boiling range greater than 300° C. are employed for lubricating oils, a group which has been subdivided, originally according to specific gravity but latterly according to viscosity, into " light," medium and " heavy " oils or into " thin," medium and " thick " lubricating oils. The refinement of these oils is effected either by sulphuric acid treatment or by solvent treatment, such as with liquid sulphur dioxide in which the unsaturated and aromatic hydrocarbons are soluble. A highly-refined petroleum oil is, therefore, one of high content of saturated hydrocarbons and, as the colour of the oil disappears during the refinement processes, the terms " white," " half-white " and " red " have been employed to designate the degree of refinement of the oil.

Of the tar oils, the most important for insecticidal purposes are

the creosote oils, which are oils of specific gravity greater than that of water, comprising the distillate of boiling range between about 180° C. and the pitching point (360–400° C., according to the type of pitch required), and the anthracene or green oils which are those fractions from which crude anthracene separates on cooling and have a boiling range of above 270° C. up to the pitching point. The predominant hydrocarbons present in such oils are of the aromatic group, though with certain types of tar oils and in hydrogenated tar oils, hydrocarbons of the first and second groups appear. With developments in hydrogenation it is possible that tar oils consisting predominantly of saturated hydrocarbons may be produced and the distinction between petroleum and tar oils, which hitherto has been definite enough for practical purposes, will become useless.

In addition to hydrocarbons, creosote and anthracene oils contain constituents soluble in acid and in alkali. The constituents removed by alkali treatment, which since they possess acidic properties are called tar acids or phenols, are mainly hydroxyl derivatives of the aromatic hydrocarbons. The content of phenols varies according to the source of the tar oil and its boiling range. They accumulate in the oils of intermediate boiling range (low-boiling creosotes) from which they are separated to form the cresylic acid of commerce. Correspondingly, the constituents removed by acid treatment are called tar bases and consist mainly of nitrogenous derivatives of the aromatic series, such as quinoline.

Historical. It is unknown when and how petroleum oils were first employed as insecticides, but kerosene was recommended in 1865 (1), soon after it came into general use, in America, as a burning oil, against scale insects of citrus. As undiluted kerosene was found to cause severe foliage and fruit injury, there was need for a method whereby the material could be applied in a less concentrated state, a difficulty partly solved by its use in an emulsified form. Lodeman (1) was of the opinion that the employment of soap solutions for emulsifying kerosene would follow naturally, for the improvement of sprays by the addition of soap as a spreader was early recognized. Other authorities (e.g. 2) have stated that the first kerosene emulsions were made with milk as the emulsifier.

The toxic activity of the petroleum products was at first thought to be related to their volatility. Shafer (3) was of the opinion that the volatile portion of kerosene and gasoline (a petroleum distillate of lower boiling-point, more familiar in England as petrol), is the effective agent and concluded that after absorption into the insect

body, the vapour becomes effective by preventing oxygen absorption by the tissues. Later (4) he showed that the vapour has an effect upon the enzymatic activity. Moore (5) found an excellent correlation between volatility and toxicity towards the Common House Fly (*Musca domestica*), the more volatile gasoline being far more effective than kerosene. Later, however, Moore and Graham (6) found that, when used as contact insecticides in emulsified form, the higher boiling fractions of the petroleum distillates are more effective than those of lower boiling-point.

Such a result is more in accordance with practical experience. Pickering (7) showed that against the eggs of Mussel Scale (*Lepidosaphes ulmi* L.) the lower boiling-point fractions of the petroleum distillates are ineffective because of their ready volatilization. He therefore recommended the use of a paraffin oil of which at least 40 per cent. has a boiling-point higher than 250° C., finally selecting a particular brand of paraffin oil called Solar Distillate, which distils almost entirely between 240° and 350° C. In the United States crude oil emulsions were frequently recommended, but there was a tendency to replace the crude oil by distillates of relatively high gravity, as illustrated by the recommendations of Yothers and Crossman (8). Although lubricating oil emulsions were, according to Smith (2), described as early as 1907, it was not until after 1922, when Quaintance (9) reported their successful use against San José Scale (*Aspidiotus perniciosus* Comst.), that their use became widespread.

The history of the introduction, into this country, of high-boiling petroleum oils is also obscure. It would appear that the superior insecticidal properties of lubricating oils were observed, independently, about 1910 by a Tasmanian fruit-grower (Hatfield, *in litt.*) who, having no kerosene, used red engine oil instead. His success was brought to the notice of an oil company who, after experiments in Australia, introduced a miscible oil containing high-boiling petroleum oils into this country in 1925. For some reason, poor emulsification according to Kent (10), spray damage according to Hiller (*in litt.*), the product proved unsuccessful. It was not until 1928, when an American preparation bearing the name of W. H. Volck, who had begun the manufacture of this product prior to 1924 (11), was introduced that interest in the high-boiling petroleum oils became general.

The value of tar as a wound dressing and of the various tar oils as wood preservatives were early discoveries, but their application

for the purpose of plant protection appears to date from about 1890. Sajó (12) found an efficient insecticide for the destruction of Mussel Scale in anthracene oil. This material he painted upon the trunk while the tree was dormant, its later application proving the cause of severe foliage injury. He recorded that Robbes, in 1889, had employed tar and turpentine oils (the latter are distillates from coniferous woods) against moth eggs. Del Guercio (13), in 1892, employed heavy tar oils in an emulsified form as a dormant spray against Woolly Aphis (*Eriosoma lanigerum*).

Various combinations of such tar distillates and an emulsifying agent, usually soap, were placed on the market under the general name of "water-soluble" carbolineums. The term "carbolineum" then referred to the various tar distillates employed as wood preservatives often with other preservatives such as zinc chloride added, but omitted from the carbolineum of the fruit-grower. The employment of carbolineum washes, in England, resulted from the introduction, by Wiltshire (14) in 1921, of a Dutch product which proved so successful that other proprietary products of a similar type quickly appeared on the market.

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The Phytocidal Properties of Hydrocarbon Oils. With these materials it is convenient to reverse the usual order of the discussion of the action of the substance on insect and on plant, for the phytocidal action of the hydrocarbon oils is the limiting factor determining their use as spray materials.

Tar oil washes were soon found totally unsuitable for application

to foliage and so great was the injury resulting from the use of early petroleum washes that their employment was limited solely to winter spraying. For dormant use, it is now known that tar oil washes must be applied before the buds begin to swell, if bud damage is to be avoided. Petroleum oils of unsulphonated residue as low as 60 per cent. (15) have been found safe, under certain conditions, for application at periods intermediate between dormancy and blossoming.

The phytocidal properties of petroleum oils to citrus foliage were examined by Gray and de Ong (16), who concluded that the constituents responsible for acute injury are removed by sulphuric acid treatment. Spuler, Overley and Green (17) showed that oils refined by either the sulphuric acid or sulphur dioxide treatments can be safely applied to deciduous foliage. These studies were extended by Green (18), by Young and Morris (19), and by Kearns, Marsh and Martin (20), and confirmation was obtained of Gray and de Ong's observation that acute oil injury is correlated with the percentage of oil removed by sulphonation, though certain oils behaved exceptionally in that they produced greater injury than was accounted for by their content of unsaturated and aromatic hydrocarbons.

De Ong (21) suggested that, in addition to unsaturated and aromatic hydrocarbons, compounds likely to oxidize, on exposure as a thin film on foliage, to acidic derivatives might prove phytocidal constituents of petroleum oils. Tucker (22) gave evidence in support of this idea and attributed the damage to the oil-soluble asphaltogenic acids formed by the oxidation of the unsaturated hydrocarbons themselves. Further, de Ong suggested that certain types of sulphur compounds would prove to be phytocidal constituents, but Green was unable to obtain conclusive evidence upon the point for, by adding to saturated hydrocarbons, sulphur compounds of a type likely to be present in a phytocidal oil, he produced greater injury, but its extent was unrelated to the amount of sulphur derivatives added.

Chronic injury by petroleum oils takes the form of a yellowing and early shedding of leaves and a delayed ripening and premature drop of fruit. With saturated hydrocarbons, de Ong, Knight and Chamberlin (23) found that oils of low viscosity are apparently safer to use on citrus than those of high viscosity. They attributed this difference to the more rapid disappearance of oils of low viscosity from the foliage, a process which they thought due primarily to

absorption rather than to volatilization. Knight, Chamberlin and Samuels (24) observed the penetration of the oil into the vascular system and showed that the recovery of citrus from the effects of oil sprays was more rapid, the lighter the oil applied. On deciduous trees, Kelley (25), who investigated the effect of hydrocarbon oils on transpiration rate, found that reduction of this rate was apparently due to the physical properties of the oil and concluded that high viscosity is associated with greater interference with metabolic processes. Spuler, Overley and Green (26), who employed the starch content of apple leaves as a measure of the effects of oil sprays on the metabolic processes, also found that the accumulation of starch in sprayed foliage increased with the viscosity of the oil applied. It may therefore be concluded that the higher the viscosity of the oil, and consequently the higher its boiling range, the more liable it is to produce injury of the chronic type.

On certain herbaceous plants, saturated hydrocarbons of the correct viscosity may cause chronic injury which appears to be associated with the interference with transpiration. Young tomato plants, especially if recently watered, assume a characteristic appearance termed œdema. Further, it should be noted that oil sprays remove the bloom from ornamental plants such as carnations and are therefore not recommended.

It is evident that the extent of foliage damage will be determined not only by the quality of the oil applied but also by the quantity retained upon the sprayed surface. This amount will be determined not only by the oil concentration of the spray applied but by the stability of the emulsion. This point was investigated by de Ong, Knight and Chamberlin (23), and by Griffin, Richardson and Burdette (27), who independently showed that the amount of oil deposited on a standard surface was greater with an unstable emulsion than with a stable emulsion. The term instability is here used not to imply instability in the spray tank but the rapid breaking of the emulsion after application. De Ong, Knight and Chamberlin decreased the stability of their emulsions by reducing the content of emulsifier, but the type of emulsifier used also affects the stability or rate of breaking of the emulsion. The interfacial surface between the disperse and continuous phases of emulsions formed by soaps, for example, resists rupture. De Ong and his co-workers therefore recommended lime casein or soda casein as more suitable emulsifiers for quick-breaking emulsions.

It may therefore be expected that the type of emulsification

will affect the phytocidal properties of the emulsion. There is practical evidence confirming this conclusion. Thus Young and Morris (19) preferred cresol-soap emulsions to casein emulsions, not only because they were more easily prepared and applied but because they were less injurious to apple leaves. Ebeling (28) concluded that liability to injury was inversely proportional to the concentration of emulsifier used.

To summarize, it has been shown that, for application to foliage, only highly refined hydrocarbon oils are suitable and that these oils should be of the minimum boiling range or viscosity and applied as emulsions of the greatest stability consistent with insecticidal efficiency.

For use upon dormant trees, the success of tar oil washes indicates that oils in which aromatic hydrocarbons predominate may be applied with safety. Bud damage is usually associated with the quantity of oil applied and factors which tend to a disproportionate concentration of oil, e.g., the presence of solid matter such as crude anthracene, the application of washes inadequately emulsified, or application in strong wind causing the repeated deposition of spray by drift, may be the primary reason for spray damage.

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The Insecticidal Properties of Hydrocarbon Oils. Phytocidal factors limit the type of hydrocarbon oil suitable for application to foliage to oils of high percentage unsulphonated residue

and of not too high a viscosity. The influence of the chemical properties of the oil upon its insecticidal efficiency is therefore of little practical importance, though it is of interest to note that de Ong's (29) suggestion that the removal of the more reactive constituents of the oil by refinement may decrease its toxicity was not confirmed by Griffin, Richardson and Burdette (30). These investigators showed that the toxicity of petroleum oils to aphides was independent of unsulphonated residue within the range examined. Spuler, Overley and Green (31) reported that, in insectary tests upon codling moth eggs, oils of the same viscosity but varying 48 per cent. in unsulphonated residue were equally toxic. Ebeling (32) concluded that, on citrus, the qualities of the spray making for greater safety to the tree also reduce insecticidal efficiency with the exception of degree of refinement. He found no correlation between degree of refinement and insecticidal properties.

The increase of insecticidal efficiency with boiling range of the oil has already been mentioned and the correlation is well shown in the results of de Ong, Knight and Chamberlin (33) upon citrus scale insects. They concluded that oils with a rather wide range of high viscosity will give complete control, but that below the minimum of this range, the lighter the oil, the less certain will be the kill. Against pests of deciduous and herbaceous plants, the action of hydrocarbon oils was critically examined by Griffin, Richardson and Burdette, employing *Aphis rumicis* as the test organism. They showed that the insecticidal efficiency of oils applied under standard conditions was independent of viscosity when the latter was above a certain minimum figure. Sprays containing oils (kerosene and gas oil) more volatile than lubricating oils required two or more times the concentration of oil to produce the same effect as the lubricating oil emulsions.

It is difficult to associate toxicity of a chemical nature with the bland saturated hydrocarbons and it is probable, as suggested by de Ong, Knight and Chamberlin (33), that the insecticidal action of such oils is dependent upon the permanence of the oil deposit left after spraying and, in the case of scale insects, upon the inability of the insect to expel the oils of viscosity above a certain minimum from its tracheal system. The efficiency of the spray will therefore be dependent, in a manner analogous to its phytocidal action, upon the amount of oil retained upon the insect after spraying. The relationship between insecticidal efficiency and the stability of the emulsion was shown by de Ong and his colleagues.

Using a highly-refined lubricating oil at 2 per cent. and lime casein at various concentrations as the emulsifier, they found that approximately 40 per cent. of the scale *Aonidiella aurantii* Maskell survived when the emulsifier concentration exceeded 0·5 per cent., whereas all were killed at emulsifier concentrations below 0·125 per cent. This increased efficiency was found to run parallel, firstly, to the greater amount of oil deposited from the emulsions of low emulsifier content and, secondly, to the average size of the oil droplets in the emulsion which was greater the less stable the emulsion. This observation was confirmed against aphides by Griffin, Richardson and Burdette (30) and by English (34), and is in accord with the results of the later fundamental work on the factors affecting the spray retention of emulsions (35). The relationship between concentration of emulsifier and insecticidal efficiency was confirmed by Smith (36) and by Ebeling (32) with blood albumin as the emulsifier and by Cressman and Dawsey (37) with soap emulsions.

The excellent penetrating properties of the oils not only permit their entry into the scale insect through the tracheæ and armour but also into the bark (38). Ebeling (39) suggested that the insecticidal efficiency might be improved if the rapid loss of oil from the plant surface by penetration into the bark could be inhibited. For this purpose he experimented with the addition, to the oil, of paraffin wax and, later (40), with oil-soluble amphipathic (see p. 82) compounds such as the triethanolamine soaps. A similar purpose underlay the experiments of Knight and Cleveland (41) who added compounds such as glyceryl oleate and aluminium naphthenate to increase the surface persistence of the oil and who reported an improved insecticidal action on deciduous fruit trees. The physico-chemical basis of the use of anti-spreaders is obscure but the related problem of the spread of oils, used as mosquito larvicides, on water has been studied by Murray (42).

For application to foliage it may therefore be concluded that the saturated hydrocarbon oil should have a boiling range, or to follow American usage, a viscosity above a certain minimum and that the emulsion should have a stability sufficient to ensure the application of a spray of uniform oil concentration yet sufficiently quick-breaking to furnish an oil deposit of the maximum insecticidal efficiency.

For dormant application, a wider range of hydrocarbon oils is available because phytocidal properties become of less importance

as a limiting factor. The main purpose of the dormant wash is the control of hibernating insects and of insect eggs. Against the former, Swingle and Snapp (43) carried out trials with petroleum oils of different characteristics and found all equally effective provided that their viscosity was above a certain minimum. They pointed out that the minimum effective viscosity varied in different parts of the United States, being lower in the more northerly States, a difference which they associated with the prevailing temperature.

The importance of viscosity and boiling range was also shown in critical work upon the physical and chemical characteristics which determine the ovicidal efficiency of hydrocarbon oils. In trials upon the eggs of the Capsid Bug, *Lygus pabulinus* L., Austin, Jary and Martin (44) showed that ovicidal efficiency was independent of the boiling range and viscosity of the oil provided, firstly, that these values were above a certain minimum and, secondly, that the content of saturated hydrocarbons was greater than a certain percentage. The second of these provisos is discussed below. Their conclusions were confirmed by field trials and are in agreement with the general experience that ovicidal properties are distributed over a wide range of high-boiling or high-viscosity petroleum oils, shown, for example, in the conclusions of Melander, Spuler and Green (45) upon toxicity to eggs of the Fruit-tree Leaf-roller (*Cacœcia argyrospila* Wlk.) and of Hamilton (46) concerning the control of Red Spider (*Oligonychus ulmi*).

These studies dealt with the ovicidal properties of petroleum oils. In the case of tar oils, the insecticidal properties of neutral oils towards the Grain Weevil, *Calandra granaria* L., were found by Goetze (47) to increase with boiling range, a conclusion also reached by Beran and Watzl (48) who, in addition to the Grain Weevil, employed larvæ of the scale *Lecanium corni* Bch. The ovicidal properties of tar oils were examined by Tutin (49) upon the eggs of *Aphis pomi* De G. and of the Winter Moth (*Operophtera brumata* L.). He found that the most toxic fraction was the high-boiling neutral oil.

The general conclusion is, therefore, that the insecticidal and ovicidal properties of hydrocarbon oils suitable for dormant use increase with boiling range or with viscosity until a certain minimum is reached. Other factors may then appear which determine a maximum figure. To give a concrete example, Martin (50), on the basis of critical experiment and general experience, concluded

that the minimum effective viscosity under winter conditions in this country and for oils of more than 60 per cent. unsulphonated residue was 125 sec. Redwood 1 at 70° F. (= , in absolute units, approximately 17·3 centistokes at 70° F.). The maximum viscosity of oils suitable for winter use is determined by considerations such as ease of handling and emulsification and the limit of 500 sec. Redwood at 70° F. (= 123·4 cs. at 70° F.) was suggested. In tar oils viscosity is not suitable as an index to boiling range, which has therefore to be defined by the minimum percentage of oil distilling, under standard conditions, at certain temperatures. The maximum boiling range of tar oils suitable for use in winter washes is fixed by their solidification at ordinary temperatures. Staniland, Tutin and Walton (51) showed that high-boiling anthracene oils which solidified on cooling were ineffective against eggs of *O. brumata.*

That the chemical character of the hydrocarbons influences insecticidal and ovicidal efficiency may be illustrated from Austin, Jary and Martin's results. The control of eggs of *L. pabulinus* by petroleum oils consisting mainly of saturated hydrocarbons was significantly better than that by tar oils consisting mainly of aromatic hydrocarbons. Allowance for the somewhat higher boiling range of the former and for the presence of constituents of a non-hydrocarbon character in the latter did not provide a complete explanation of the difference and it was suggested that oils of a low content of saturated hydrocarbons have inferior ovicidal properties towards these eggs. Other evidence brought forward by these investigators indicated that this inferiority may not become of practical importance until the unsulphonated residue of the oil falls below 60 per cent. by volume. The conclusion that a certain content of unsaturated and aromatic hydrocarbons may not affect the efficiency of an oil is in agreement with the results of Spuler, Overley and Green (31), who showed that refinement to a stage beyond that represented by 50 per cent. unsulphonated residue was not necessary with petroleum oils for use against the eggs of *C. argyrospila*, and of Swingle and Snapp (43), who found unsulphonated residue of no effect upon the toxicity of the petroleum oils they used against *Aspidiotus perniciosus.* The reduction of ovicidal efficiency when the character of the hydrocarbons is changed from saturated to aromatic is most strikingly shown by practical experience of Red Spider (*Oligonychus ulmi*) control. Whereas petroleum oils exert a degree of control when applied as

winter washes against this pest, the tar oils are useless (see, e.g., 52).

Generalizations on the relative efficiency of saturated and aromatic hydrocarbons of similar boiling range are complicated by the fact that, against eggs of Aphididæ and Psyllidæ, the saturated hydrocarbons are devoid of ovicidal properties. To explain this apparent reversal of the conclusions reached in the preceding paragraph, Staniland, Tutin and Walton (51) suggested that the ovicidal properties of hydrocarbon oils are exerted in two ways : firstly, a physical " stifling " action associated with the permanence of the oil film over the insect egg and to which is due the ovicidal properties of hydrocarbon oils upon geometrid and capsid eggs but which has no effect upon aphid and psyllid eggs ; secondly, a chemical toxic action peculiar to tar oils and to which is due their action upon aphid and psyllid eggs.

The first hypothesis, of a " stifling " action, is not only in accord with the conclusion that the hydrocarbon should be liquid, high-boiling and non-volatile but has been experimentally verified by Powers and Headlee (53) on eggs of the mosquito *Aides ægypti* L. They found that the main cause of death was oxygen starvation rather than the accumulation of carbon dioxide within the oil-covered egg, and concluded that the variations in ovicidal properties of the petroleum oils examined were probably factors such as too short a period of oil retention or the failure of the oil to make a complete seal. Further the hypothesis may explain the superiority of the saturated hydrocarbons over the unsaturated and aromatic hydrocarbons for the latter, being more chemically reactive, may form water-soluble derivatives removed by rain. The effect of water on the weathering of creosote was found, by Gillander *et al.* (54), to be confined mainly to the removal of the more polar compounds present and to hydrocarbons distilling below 270° C.

The predominant group of polar compounds present in aromatic oils is the phenols, and it was observed by Tutin (49) that their removal increases the toxicity of tar oils to eggs of *O. brumata.* His conclusion was confirmed by the extensive field work of Staniland, Tutin and Walton (51) upon *P. rugicollis* and by the results of the laboratory trials of Austin, Jary and Martin (44) upon eggs of *L. pabulinus.*

The second hypothesis of a chemical toxic action to which aphid and psyllid eggs are peculiarly susceptible was examined by Austin,

Jary and Martin (44) on *Psyllia mali* and by Kearns, Martin and Wilkins (55) on A. *pomi*. The relationship between volatility and ovicidal properties does not follow as a corollary to this hypothesis as it does to the fruit but the earlier observation of Tutin, that ovicidal properties to A. *pomi* ascends with distillation range, was confirmed. Further, it was shown that, in the oils examined, toxicity was associated with the content of aromatic hydrocarbons as assessed by solubility in dimethyl sulphate. This criticism has provided a satisfactory test in the standardization of tar-oil products (see e.g. 56) but, theoretically, it implies an absence of marked differences in ovicidal action among the compounds which constitute high-boiling hydrocarbons soluble in dimethyl sulphate. Such differences were not found by Kearns, Martin and Wilkins but every new source of hydrocarbons requires investigation for the discovery of differences would greatly facilitate research on the isolation of the compounds responsible for ovicidal action.

The influence of the polar compounds present in tar oils on the ovicidal action of the chemical type appears to be slight. The tar bases examined by Shaw and Steer (57) exhibited ovicidal properties, outstanding in nicotine, but not of an order which makes them of importance at the low concentrations present in tar oils. Though Tutin (49) stated that the presence of phenols reduced the toxicity of tar oils to *A. pomi*, no confirmatory evidence of this observation is available.

Contrary to the results obtained by the application of petroleum oils to foliage, the influence of the stability of the emulsion does not appear to affect markedly the ovicidal efficiency of winter washes. Austin, Jary and Martin (44) and Steer (58) obtained a similar control of *L. pabulinus* by a tar-petroleum oil mixture whether emulsified by Bordeaux mixture or by the two-solution oleic acid method. Speyer (59), who examined the action of a number of proprietary preparations upon the eggs of *P. mali*, found no relationship between toxicity and the stability or surface tension of the diluted washes.

Summarizing, it may be concluded that the insecticidal efficiency of hydrocarbon oils applied as dormant washes is determined by two sets of factors. When employed against insects or eggs susceptible to a " stifling " action, the oil should have a boiling range or viscosity above a certain minimum and should contain the maximum practicable of saturated hydrocarbons and the minimum of phenols. When employed against insect eggs susceptible to

the chemical toxic action, the content of aromatic hydrocarbons should be above a certain minimum. By the use of a suitable combination of petroleum and tar oils it becomes possible to control adequately both types of insect eggs, provided that the total oil concentration of the wash is not greater than that causing spray damage.

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THE GLYCERIDE OILS AND SOAPS

The use, as spray supplements, of the glyceride oils, known more familiarly as animal and vegetable oils, has already been reviewed (p. 81). The oils themselves, in addition to their virtues as spreaders and stickers, possess insecticidal properties. Staniland (1), attempting to find a cheap substitute for nicotine, tried various vegetable oils as spring and summer sprays. He selected rape and linseed oil on account of their easier emulsification with soft soap, a property now known to be determined by the content of free fatty acid present in the oil, but found the latter unsuitable owing to its rapid " varnishing " after application. The rape oil emulsion was found of satisfactory toxicity and proved less phytocidal than a petroleum oil emulsion tested at the same time. The ovicidal properties of vegetable oil emulsions were examined by Austin, Jary and Martin (2) against the eggs of *Lygus pabulinus* and they were shown to be intermediate in efficiency between the high-boiling petroleum oils and anthracene oils. On the score of cost, the gylceride oils cannot compete, in this country, with petroleum oils as winter washes, whilst for summer use, hydrocarbon oils are more effective against Red Spider. For certain purposes, e.g. as supplements for copper fungicides, the hydrocarbon oils are more suitable than the glyceride oils, though the latter are of particular value when direct fungicidal properties are required.

The soaps, which are the alkali salts of the higher fatty acids, have long been known to possess contact insecticidal properties. Thus Lodeman (3) recorded that D. Haggerston, in 1842, employed a whale-oil soap against aphis, red spider and thrips. This action was at first attributed to the caustic action of the alkali constituent of the soap, but Siegler and Popenoe (4) have shown that the acid constituent possesses a definite insecticidal action. Employing a series of normal saturated monocarboxylic fatty acids, they observed a striking increase in toxicity towards certain aphides as the series is ascended, the maximum toxicity being reached at capric acid, $C_9H_{19}COOH$. Their results have been confirmed by Tattersfield and Gimingham (5), who showed that the relative toxicities to *Aphis rumicis* of the fatty acids increase with molecular weight as the series is ascended from acetic to undecylic acid, $C_{10}H_{21}COOH$, and that beyond this point there is a fall in toxicity, the acids above tridecylic acid, $C_{12}H_{25}COOH$, showing but a slight toxic action. The sodium salts of these acids were in most cases much less toxic

than the corresponding acids, but the difference was not so marked with the ammonium soaps, which may be due to their readier hydrolysis, an action which results in the liberation of the fatty acid.

Similar investigations were made by Dills and Menusan (6), who found capric acid and lauric acid, $C_{11}H_{23}COOH$, the most toxic of the saturated fatty acids towards *A. rumicis* and *Macrosiphum rosæ* L. Of the potassium soaps, the laurate was the most toxic of the saturated derivatives but was surpassed by the oleate. Sodium oleate was found by Tattersfield and Gimingham to be as toxic as oleic acid, an unsaturated acid which was slightly less effective than the more toxic of the saturated acids.

This example of the dependence of insecticidal properties upon molecular structure has attracted theoretical consideration. Tattersfield and Gimingham were unfortunately unable to determine directly the median lethal dose (see p. 300), but, by plotting the logarithm of the reciprocal of the molecular concentration necessary to give 100 per cent. mortality, against the molecular weight of the acid, O'Kane *et al.* (7) showed that Tattersfield and Gimingham's results gave points lying on a straight line. It would therefore seem that an absorption process is involved in the gradual increase of toxicity with molecular weight, or, more accurately, the length of the carbon chain, until a point is reached when other factors which inhibit toxicity come into play. Tattersfield and Gimingham examined a number of the physical properties of the saturated fatty acids which might be involved in the adsorption process and, in particular, adduced evidence of a relationship between toxicity and the partition coefficient (see p. 304) of the acid between olive oil and water. O'Kane and his colleagues showed that the surface activity of the fatty acid, which they employed as a measure of surface adsorption, when plotted on a semi-logarithmic scale against molecular weight also gives a straight line. In a later paper, O'Kane and Westgate (8) established a relationship between surface activity (as measured by contact angle upon paraffin wax or upon the integument of larvæ of the Meal Worm, *Tenebrio molitor* L.) and molecular weight of the sodium soaps of the saturated acids similar to that between insecticidal properties and molecular weight, the most active soap over the range of concentrations examined being sodium laurate. They pointed out, however, that sodium laurate may not be necessarily the most effective of the saturated fatty acid soaps against all insects, for the nature of the integument, and hence the contact angle, may not be the same for all insect species.

The relationship between advancing contact angle (and surface tension) and the insecticidal properties of soap solutions was also examined by Dills and Menusan, who found that, whereas the least toxic of the soaps could be distinguished by surface tension or contact angle measurements, neither of these measurements is a good index of the probable contact insecticidal properties of the soap. In their comparison, however, they included a number of soaps not of the saturated series and it is noteworthy that, of the saturated fatty acid soaps included in their trials, that which showed the lowest contact angle at one-sixth per cent. concentration was sodium laurate.

Of attempts to extend the use of soaps and fatty acids as practical spray materials, mention may be made of the recommendation by Siegler and Popenoe (4) of the product known as " Doubly distilled coconut fatty acids," which on analysis was found to contain a high percentage of capric and lauric acids. This substance, of m.p. 27° C., is stable in petroleum oil emulsion, is readily obtainable and, at a strength yielding similar results, is about one-fourth the cost per gallon of the nicotine spray. The most serious limitation to the employment of the fatty acids themselves is their high phytocidal activity, observed by Martin and Salmon (9). Dills and Menusan found that the most phytocidal of the fatty acids were capric and lauric acids and that an increase of molecular weight beyond this point was accompanied by a decrease in phytocidal properties. In the case of the potash soaps, however, they found no correlation between insecticidal and phytocidal properties, plant injury decreasing with molecular weight.

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QUASSIA

Quassia is the wood of two trees of the family Simarubaceæ, that known commercially as Jamaica quassia is *Picrasma (Picræna) excelsis* (Swz.) Planch., and that known as Surinam quassia is *Quassia amara* L. Other woods having bitter principles similar to or identical with those of the above are detailed by McIndoo and Sievers (1).

The extract of quassia wood appears to have been first used against the Hop Aphis (*Phorodon humuli* Schrenk.) about the year 1884 (2). Whitehead (3) recorded that hop washing, using a quassia-soft soap extract, had by 1890 become a regular feature of hop cultivation.

The extraction of the toxic principles, the quassins and picrasmins, was examined by McIndoo and Sievers, who showed that the best extraction is secured by the use of a cold soap or lye solution. It appeared that a decomposition of the toxic constituents by the alkali occurred on heating.

The action of the quassins upon the insect was examined by McIndoo and Sievers, who showed that they can act neither through their vapour nor as stomach poisons. By penetration of the spiracles the toxic material reaches the nervous tissue, where it kills by its slow action on the nerve cells. Whereas nicotine acts quickly by paralysis, quassin causes no noticeable paralysis, the aphides become inactive and die in a state analogous to the " coma " of higher animals. These workers found further that quassin appears to be effective only against certain species of the aphides and is of little use against other insects. Although Parker (4) found that the toxicity of quassin compares favourably with nicotine sulphate against *P. humuli*, quassia extracts have now been generally replaced by nicotine.

Interest in quassia has, however, recently been revived by the observation of Thiem (5) of the potent action of the extract on certain species of sawfly (*Hoplocampa* spp.), an observation confirmed by Petherbridge and Thomas (6).

The constitution of the active constituents has not yet been elucidated, but Clark (7) has separated the quassins to two isomers for one of which he has retained the older name and the other he has called neoquassin. From *P. excelsis* he isolated one picrasmin. As these three principles have the same empirical formula, $C_{22}H_{30}O_6$, and each contains two methoxy groups, one of which is

removed by mild acid treatment to form the same semi-demethoxy-quassin, their structures must be very similar.

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THE SULPHUR GROUP

Sulphur. It is possible that the first use of sulphur as an " insecticide " was its employment to cure scabies, a human skin affliction due to the mite *Sarcoptes scabiei*. Similar diseases of animals such as sheep scab, due to a related mite *Psoroptes communis*, have for long been treated with sulphur in various forms. As it is probable that these pests were recognized before those closely-related organisms responsible for certain plant diseases, it may well be assumed that the application of sulphur to the purposes of Plant Protection is of later date. These organisms are of the Arachnida, of which those most serious as plant pests are the Gall Mites (Erio-phyidæ) and Red Spiders (Trombididæ). Against these pests sulphur has proved a most valuable " insecticide."

As the forms of sulphur available for application as sprays and dusts have already been discussed (p. 104), attention need only be directed to the necessity for using finely-ground products. The relationship between insecticidal efficiency and degree of fineness was demonstrated by McGregor (1) in the use of sulphur for the control of the Citrus Thrips, *Scirtothrips citri* Moult.

The mode of action of sulphur upon the mites has been examined by Lees (2). By placing twigs of black currant bearing Big Bud, caused by *Eriophyes ribis*, within bell-jars coated on the inside with sulphur, he found that the mites upon the buds were rapidly killed. From the conditions of his experiments, the toxic agent must have been volatile and Goodwin and Martin (3) showed that it is sulphur in a gaseous form, the volatility of sulphur at ordinary temperatures being sufficient to affect the mite. It is suggested that regions in which sulphur, as distinct from the polysulphides, has been found of service as a true insecticide are tropical or sub-tropical. Further,

it should be noted that sulphur and the polysulphides are not effective ovicides and, when the generations of the pest overlap, it is necessary to make two or more applications.

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Lime Sulphur.   Lime sulphur and, in particular, liver of sulphur have long been employed as acaricides and it is probable that they function, primarily, through elementary sulphur deposited by the decomposition of the polysulphides present.

As a true insecticide, lime sulphur was first used as a plant spray in 1886 by F. Dusey (4), who accidentally discovered that a sheep-dip—a lime-sulphur-salt mixture known as California wash—was efficient for the control of San José Scale (*Aspidiotus perniciosus*). The mixture rapidly became the principal means of control of the pest and modifications quickly came into favour.   The addition of salt, for example, which had been added possibly because, by raising the boiling-point of the suspension, it was thought to promote the interaction of the lime and sulphur, gradually fell into disuse. Pierce (5) and Henderson (6) reported that its addition was unnecessary for insecticidal purposes.   The use of commercially prepared lime sulphurs has successfully replaced the older laborious process of home manufacture.

The chemistry and the action of such lime sulphurs upon the plant have already been discussed.

The properties to which lime sulphur owes its insecticidal value against scale insects were examined by Shafer (7).   Firstly, he found that the spray was able to soften the wax around the edge of the insect and, on drying, to cause it to stick to the plant.   The young insects were killed by this sealing of the scale covering of the mother.   Hartzell and Lathrop (8) confirmed the softening action upon the wax of *A. perniciosus*, but did not observe the adhesion of the insect to the bark.   Secondly, Shafer found a more important factor in the oxygen-absorbing qualities of lime sulphur. But O'Kane and Conklin (9) showed that the evolution of hydrogen sulphide practically ceases within six hours of exposure of the lime sulphur spray deposit.   As the greater part of this hydrogen sulphide is produced by the action of carbon dioxide upon the poly-

sulphides, it may be concluded that the oxygen-absorbing properties of the lime sulphur deposit are fugitive. It is questionable, in view of Melander's (10) statement that the toxicity of lime sulphur to *A. perniciosus* is not exerted until ten days after application, whether Shafer's conclusion can be substantiated. Finally, Shafer (11) found that those waxy membranes which have been thoroughly soaked with lime sulphur are less permeable to oxygen than untreated membranes. He suggested that this decreased permeability might contribute to the toxic action of lime sulphur.

Hartzell and Lathrop (8) considered that the volatile products formed by the decomposition of lime sulphur possessed toxicity especially to young scale insects. O'Kane and Conklin (9) showed that neither hydrogen sulphide nor sulphur dioxide could be regarded as the toxic agents against *A. perniciosus* or *Lepidosaphes ulmi*. The toxicity of lime sulphur may therefore be ascribed to the polysulphides or the sulphur formed by the decomposition of these compounds. As calcium thiosulphate appears to have little insecticidal value (7, 12), a measure of the insecticidal and acaricidal efficiency of lime sulphur is given by the polysulphide content.

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Barium Polysulphide. The extensive use in the United States of lime sulphur as a scalecide has led to attempts to introduce a dry material of equal value. The difficulties of transport and storage of lime sulphur are a serious disadvantage. Dry-mix sulphur lime, though a more or less effective substitute for fungicidal purposes, has little value as an insecticide. Liver of Sulphur is too hygroscopic a solid to be satisfactory. Scott (13) therefore proposed the use of barium polysulphide. Barium tetrasulphide can be prepared as reddish-yellow crystals, $BaS_4.H_2O$, relatively stable and readily soluble in cold water. The actual powder, placed on the market under the name B.T.S., contains in addition barium thiosulphate

and a certain amount of free sulphur, which appears however to be soluble in barium tetrasulphide solutions forming higher poly-sulphides. Scott found the material to keep well, though slowly oxidized by long exposure to air. He not only proved, by field trial, that the substance is as efficient as lime sulphur, but obtained results which indicated that it is less likely to injure vegetation. Barium polysulphide does not appear, however, to be used at all extensively, perhaps because of the poisonous nature of barium compounds. A German product, a yellowish-black powder sold under the name " Solbar " as a fungicide and scalecide, appears to be a related product.

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Selenium. In view of its relationship to sulphur, selenium may be considered under this head. It was reported, in 1933, by Gnadinger (14) that selenides, prepared by the solution of selenium in alkali or alkali sulphide solutions, are toxic to the Tetranychid mites (Red Spiders). The form most suited to glasshouse plants was found to be a solution of selenium in potassium ammonium sulphide solutions in proportions corresponding to the formula $(KNH_4S)_5Se$. A 30 per cent. solution of this preparation was placed on the market under the name " Selocide."

According to Gnadinger, selocide appears to be specific in action and without marked insecticidal properties to true insects. He reported a series of successful trials, but little confirmatory evidence has been published. A serious disadvantage is the toxicity of selenium compounds to man and to stock, not so much directly as through the ready absorption of the element by the plant to which it confers a high degree of toxicity. The interest aroused by the selenium problem of soils (see 15) has tended to discourage the further investigation of the selenium spray materials, except on crop plants not used for food. Mason and Phillis (16), for example, reported that, by the inclusion of selenium in the nutrient solutions, cotton grown in sand culture was rendered resistant to the insect attack. Maris, Neiswander and Sayre (17) employed the same method to overcome the difficulty of the control of Red Spider on wheat grown for physiological studies in the glasshouse.

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THE ORGANIC THIOCYANATES

Murphy and Peet (1), in a study of the insecticidal properties of various organic radicals, found the most promising to be the thiocyanate group,—S—C≡N. In their published account these workers did not specify the actual compound used but reported that an aliphatic thiocyanate was highly toxic to *Aphis rumicis*, and, in a second paper (2), successful trials of the same compound upon the Mealy Bug *Pseudococcus citri* and its eggs are recorded. Compounded products based on this thiocyanate were placed on the market under the name " Lethane " and, in 1936, Murphy (3) described the active constituent as β-butoxy-β-thiocyanodiethyl ether, $C_4H_9O.CH_2.CH_2O.CH_2.CH_2.SCN$ (*n*-butyl " Carbitol " thiocyanate).

Bousquet, Salzberg and Dietz (4) examined the insecticidal properties of a number of aliphatic thiocyanates, selecting a series of the thiocyanates of the saturated even-carbon fatty alcohols from ethyl to cetyl alcohol. They established the marked influence of the alkyl radical upon the toxicity of these compounds to various aphides, thrips and red spider. In all cases the C_{12} member, μ-dodecyl (μ-lauryl) thiocyanate, $CH_3(CH_2)_{10}CH_2.SCN$ was found to be the most toxic.

Other organic thiocyanates, in particular aromatic derivatives, were examined by Hartzell and Wilcoxon (5), who showed that 3-thiocyanopropyl phenyl ether, $SCN.CH_2.CH_2.CH_2O.C_6H_5$, was highly toxic to *A. rumicis*, and superior to the corresponding halogen derivative. Subsequently (5) they found trimethylene dithiocyanate, $SCN.CH_2.CH_2.CH_2.SCN$, not only more toxic than the propyl phenyl ether derivative to *A. rumicis* and effective against a wide range of insects, but less phytocidal over the range of plants tested.

In searching for an ovicide suitable to replace the highly phytocidal tar oils of the tar-petroleum wash, Kearns and Martin (6) found μ-dodecyl thiocyanate (lauryl rhodanate) toxic to eggs of *A. pouri* and *Psyllia mali*, a result confirmed by Shaw and Steer (7) who also found the thiocyanates of the corresponding secondary alcohols less ovicidal. Hey (8), Shaw and Steer (7) and Kearns and Martin

(9) reported successful trials of butyl " carbitol " thiocyanate which has appeared as an active constituent of a proprietary winter wash. The nature of the insecticidal action of the thiocyanates was investigated by Hartzell and Wilcoxon (5) who, from the histological examination of larvæ of *Tenebrio molitor* killed by 3-thiocyano-propyl phenyl ether, concluded that death was due to injury to the central nervous system, accompanied by paralysis. Studies of the toxicity of the thiocyanates to warm-blooded animals, reviewed by Murphy (10) and by Cameron, Doniger and McKinney Hughes (11), indicate that the compounds tested are relatively harmless. Because of this and for psychological reasons, the older name rhodanate has been adopted by our manufacturers for the thiocyanate radical.

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THE DINITROPHENOLS

In their pioneer work on systematic lines of insecticidal properties, Tattersfield and his colleagues (1) included derivatives of the aromatic hydrocarbons, and it is of interest to note the relationships of chemical constitution and ovicidal properties elucidated by these workers. They found but little difference in the toxic values of phenol and the three isomeric cresols towards the eggs of the Purple Thorn moth, *Selenia tetralunaria* Hufn., but observed a great increase in the toxicity of these compounds when nitro-groups are introduced. The introduction of a second nitro-group gave a further increase in toxicity, but the relative position of the two nitro-groups had some effect. Further nitration led to a decrease in toxicity. Accepting the symbols $<$, $>$ to mean " less toxic

than " and " more toxic than," Tattersfield gave the following scheme :

To eggs of *Hadena oleracea* L. :

Benzene < nitrobenzene < *m*-dinitrobenzene > 1:3:5-trinitrobenzene.

To eggs of *S. tetralunaria* :

o-nitrophenol = *p*-nitrophenol < 2:4-dinitrophenol > 2:4:6-trinitrophenol
3-nitro-*o*-cresol = 5-nitro-*o*-cresol < 3:5-dinitro-*o*-cresol > trinitro-*m*-cresol.

The 3 : 5-dinitro-*o*-cresol was found to possess so high an ovicidal value that field trials were carried out with this compound. The results (2) showed the practicability of using both this compound and its salts as dormant spray materials. The potassium salt had been introduced some time before as an active constituent of " Antinonnin " (see p. 172) but its use was limited by its phytocidal properties which are, however, not objectionable for winter wash purposes. The poisonous and explosive properties of the dinitrocresol render it unsuitable for sale as such to the grower, but these difficulties are largely overcome if the product is placed on the market in compounded forms merely requiring dilution to spray strength. Only recently have manufacturers followed up Tattersfield's work by the introduction of compounded winter washes based on dinitrocresol. Successful trials with these products have been reported by Blÿdorp (3), Hey (4) Shaw and Steer (5), and Kearns and Martin (6). In these products the acid is dissolved in petroleum oil whereby the ovicidal properties of the latter are combined with the toxic properties of the cresol against eggs of Aphididae and Psyllidæ and against moss and lichen.

The low solubility of the cresol in petroleum oils of the type used as ovicides may prove a handicap in compounding, a possible reason for the further survey of related phenols by Kagy and Richardson (7). These workers reported that the compound which showed consistently the highest toxicity was 2 : 4-dinitro-6-cyclohexyl-phenol (U.S.P. 1880404), a compound which differs in constitution from the cresol only in the substitution of the methyl ($-CH_3$) group of the latter by the cyclohexyl ($-C_6H_{11}$) group. The introduction of this heavier hydrocarbon group would, presumably, increase the oil solubility of the compound. The results of spray trials of washes containing this compound, at one time designated by the symbol DNOCHP, have been consistently successful (see 8) and the observation of synergy (see p. 300) between the phenol and the oil by Kagy and Richardson has been verified by Bliss (9).

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MISCELLANEOUS CONTACT INSECTICIDES

Empirical selection, which revealed tobacco, derris, pyrethrum and quassia, has left a long list of plants reputed to possess insecticidal properties, of which Roark (1) cited no less than 180 species. Many of the materials he mentioned, however, are used more to prevent insect attack, as, for example, Rosemary, a herb used to repel clothes moth, and Eucalyptus, the scent of which is said to keep away mosquitoes. Of those reputed to possess actual insecticidal properties, McIndoo and Sievers (2) tested the action of various preparations derived from 54 species upon various insects. Included in their trials were certain of the plant species already discussed, but of the others, **Stavesacre** (Lousewort) and **Tomato** warrant mention. Davidson (3) found the oil and alkaloids from the seeds of Stavesacre (*Delphinium staphysagria*, L.) and Larkspur (*D. consolida*, L.) insecticidal.

Decoctions of tomato leaves and stems (*Lycopersicum esculentum* L.) have been used in Russia (4) against caterpillars of the Large Cabbage White Butterfly (*Pieris brassicœ*), whilst Blin (5) found an extract of tomato stems in potash lye a substitute for nicotine ; the tobacco and tomato are both solanaceous plants. McIndoo and Sievers found the alcoholic and ether extracts of tomato vines very effective against flies and bees.

It is to synthetic rather than plant products that attention is now being paid in the search for better contact insecticides. The discovery of neonicotine, of the dinitrophenols and of the organic thiocyanates is an indication of the value of such surveys. One other may be mentioned, that of the organic amines. These compounds have been the subject of much physiological research and were first studied, from the insecticidal aspect, by Tattersfield

and Gimingham (6).   Their work did not reveal a potent insecticide but provided valuable pointers to an effective amine, a possibility strengthened by Richardson and Shepard (7) who, in an
investigation of the degradation production of nicotine, obtained
evidence that the substitution of the simple aliphatic amines in the
3-position of pyridine might furnish a compound of high insecticidal potency.

Kearns and Flint (8) followed up this earlier work.   Aniline, an
aromatic amine $C_6H_5NH_2$, had been found by Tattersfield and
Gimingham but slightly toxic to *A. rumicis*, but it was known
(6, 9) that hydrogenation of bases such as pyrrole and pyridine
increased their toxicity.   Kearns and Flint therefore began their
survey with the hydrogenation product of aniline, *cyclo*hexylamine,
$C_6H_{11}NH_2$, a readily available and relatively cheap material.
The observations of Tattersfield and Gimingham on the effects of
substitution in the hydrogen atoms attached to the nitrogen of
aniline led Kearns and Flint to examine the N-substituted derivatives of *cyclo*hexylamine.   Substitution of the first hydrogen of
the $-NH_2$ group by an alkyl group tended to produce greater
toxicity than various acyl, aryl or aralkyl substitutions, and, in
general, the toxicity increased with the size of the alkyl groups
(cf. the organic thiocyanates, p. 222) up to and including the
octyl group $-C_8H_{17}$.   The additional substitution of the second
hydrogen of the $-NH_2$ group by an acidic group such as the benzoyl
or acetyl radicals further increased toxicity.   Of the derivatives
tested, Kearns and Flint selected

$$\text{N, N-amyl-benzoyl-}cyclo\text{hexylamine} \quad C_6H_{11}N\underset{\diagdown COC_6H_5}{\overset{\diagup nC_5H_{11}}{}}$$

$$\text{and} \quad \text{N, N-amyl-acetyl-}cyclo\text{hexylamine} \quad C_6H_{11}N\underset{\diagdown COCH_3}{\overset{\diagup nC_5H_{11}}{}}$$
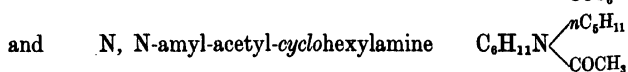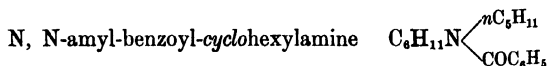
as highly toxic both to the aphid *Myzus porosus* Sand. and the
Red Spider *Tetranychus telarius* L.   These two compounds were
found to be rather injurious to foliage, a property which Kearns
and Compton (10) traced to the acidic acyl group.   The substitution
of the benzoyl group by the benzyl group to give

$$\text{N, N-amyl-benzyl-}cyclo\text{hexylamine} \ C_6H_{11}N\underset{\diagdown CH_2C_6H_5}{\overset{\diagup nC_5H_{11}}{}}$$
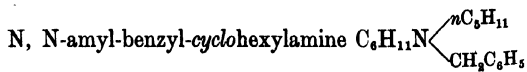
reduced phytocidal and increased insecticidal properties.   Kearns
and Compton found that the efficiency of this liquid was markedly

dependent on the type of emulsifier used, but further evidence of the ·practical value of the compounded product is not yet available.

The so-called cover washes, which include the lime washes intended to coat the insect egg which will mechanically prevent egg-hatching, and the caustic washes used as tree-cleansers (11) have been superseded by the hydrocarbon oil washes.

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INSECTICIDES *(continued)*

DETERRENT ACTION

In discussing the stomach poisons, stress has been laid upon the toxic qualities of the insecticide. The aim underlying their use has been to secure the consumption, with the plant tissue, of sufficient poison to prove toxic. But, if the insect is deterred in some way from eating sufficient of the treated foliage to produce this result, a protective action of the insecticide is obtained. It is not always necessary to presume any special action characteristic of the insecticide used other than the gritty nature of the deposit, for it has been shown that dust or dirt on the plant surface will exercise a similar deterrent action. Against the Flea-beetles (Halticinæ), for instance, Petherbridge (1) recommended rolling while the dew is on the plant or the driving of sheep over the infested area. These methods are effective, probably because of the dust raised which, settling on the young plants, deters the flea-beetle from continuing its attack.

In much the same way, it has been found that Bordeaux mixture may act as a deterrent insecticide. Against the Red-headed Flea-beetle, *Systena frontalis* F., Hawley (2) found not only that the combined Bordeaux mixture-lead arsenate spray and lead arsenate alone acted as repellents but that sulphur and fertilizers dusted on the leaves have a repelling action. The deterrent action of Bordeaux mixture is of the greatest use in the control of "Hopper burn" of potato. The propagation of this disease is due, as Ball (3) has shown, to the activities of the Potato Leaf Hopper *Empoasca mali* Le Baron. The control of Hopper burn is therefore reduced to the prevention of the attack of the Leaf Hopper. Martin (4) reported that, for potatoes, Bordeaux mixture is the most satisfactory spray, as it acts not only as a fungicide but as a repellent of insects, particularly the leaf hopper.

To prevent the loss caused by graminivorous birds from seed beds, the treatment of the seed with deterrent materials has often

been suggested. No scientific work appears to have been carried out in this connection, but there exist a number of more or less home-made deterrent seed steeps. Such materials usually contain red lead or some bitter agent, such as aloes, quassia, or tarry substances, with which the seed is coated prior to sowing.

The use of deterrents has no wide practical application, and it is obvious that if by a treatment involving an equal expenditure it is possible to kill the insect, the latter is to be preferred. Thus a toxic material such as an arsenical or nicotine is frequently added to Bordeaux mixture when employed as a deterrent, for half a kill is better than none.

Further, with seedling plants, such insecticides are of little use because the seedling is unable to spare the fragment of its tissue bearing the deterrent without suffering severe injury. Newton (5) found here a special difficulty in the control of Flea-beetles by such deterrents : the single bite of the insect, essential to secure the deterrent action, was sufficient to cause the death of the seedling. In such cases, the closely related practice of employing a material the presence of which prevents the attack by its action at a distance may be used. The use of such repellents will be discussed under the heading of " Trapping " and they may be distinguished from deterrents in that they provide, when successful, a complete protection to the plant, whereas deterrents involve, in their action, at least some slight injury to the plant.

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COMBINED WASHES

Combined washes may be classed into two groups, firstly, those containing components employed against one or more pests of the same general type. Such sprays may be regarded more as means of securing a more effective spray by using two toxic agents instead of one, a familiar example being the use of nicotine and soft soap

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* The distinctive use of the terms " deterrent " and " repellent " is made solely for convenience : the terms as generally employed are synonymous.

against soft-bodied suctorial insects. Not only does the soft soap
by its action as a spreader render the nicotine more effective but
it may exert a direct insecticidal action. It may be that the
combined effect of the two toxic agents is greater than that predicted
from the toxicities of the individual compounds, a synergistic effect
noted in the dinitro-phenol-petroleum oil combination (p. 224).

To the second group belong those sprays intended to control
pests of different types such as the fungicide active against both
endophytic and ectophytic fungi, an example of which is mentioned
on p. 151. The general case is the combination of a direct-acting
toxic material with a protective insecticide or fungicide, a possi-
bility which appears to have first been investigated by Weed (1).

It is obvious that the simultaneous application of a fungicide
and insecticide will result in considerable saving not only in labour
but in time, a factor frequently of greater importance. This
economy must not be purchased, however, at the expense of serious
interference with the fungicidal or insecticidal properties of the
components of the spray or of a pronounced increase in the risk
of spray injury. These requirements limit the number of possible
combinations and there has arisen thereby a rough division of
such mixtures into " compatible " and " incompatible " sprays (2).
In many cases it is evident from a consideration of the chemistry
of the components that the mixture is impracticable ; for example,
the use of arsenicals with oil emulsions emulsified with soap or
containing alkali. In other cases, the results of the interaction
are not so obvious and extended field trials may be necessary to
determine the practicability of the combined wash. Further, it is
necessary that the correct times of application of the components
of the combined spray should coincide and that the method of
application of the components should be the same. The latter
problem becomes acute in the combination of a direct with a
protective spray material. As the majority of the direct insecticides
and fungicides require application in copious amounts if a well-
wetting spray is to be obtained, the supplements selected for the
combined wash should give maximum retention when so applied.

In the combined protective spray, this physical requirement
presents no fundamental difficulty but the problem of chemical
compatibility may be involved, as in lime sulphur-lead arsenate
mixture, used for the simultaneous control of Apple Scab (*Venturia
inæqualis*) and Codling Moth (*Cydia pomonella*). That a reaction
occurs on mixing lead arsenate with lime sulphur is demonstrated

by the change of colour of the particles of lead arsenate, which turn a reddish-brown rapidly changing to black. Goodwin and Martin (3) examined not only the effects of this reaction on the fungicidal and insecticidal properties of the spray and on the likelihood of arsenical injury, but also the influence of the addition of supplements on this reaction.

In the discussion of the chemistry of lime sulphur (see p. 116), the formation of sulphuretted hydrogen by hydrolysis of the calcium polysulphides was mentioned. It would appear that the interaction of lime sulphur with diplumbic hydrogen arsenate is due primarily to this sulphuretted hydrogen and that the extent of the reaction is governed by the rapidity of the decomposition of the calcium polysulphides and of the removal of the hydrogen sulphide. Part of the lead arsenate is converted to lead sulphide and a corresponding amount of arsenic is converted to calcium arsenate and thioarsenates, salts which being more easily rendered soluble than the original lead arsenate cause the appearance of an increased amount of arsenic in solution. If to the combined spray a supplement such as casein or gelatine be added, the escape of the sulphuretted hydrogen is inhibited, a retention by which the extent of the hydrolysis of the calcium polysulphides is reduced and the decomposition of the polysulphide compounds retarded. A greater proportion of the lead arsenate is thereby decomposed and the amount of arsenic converted to. a more soluble form increased. If, however, lime casein be the spreader employed, the free lime present will cause the precipitation of soluble arsenic in the manner already described (see p. 165). Moreover, the presence of free calcium hydroxide will interfere with the decomposition of the calcium polysulphides, resulting in an increased formation of calcium thiosulphate and a corresponding reduction of the sulphur freed by the decomposition of the polysulphides. It is possible that an intermediate stage in this reaction is the interaction of the calcium hydroxide and the sulphuretted hydrogen which not only leads to the formation of further sulphide compounds, the oxidation of which yields calcium thiosulphate, but also causes a more rapid removal of the sulphuretted hydrogen and a decreased decomposition of the original lead arsenate.

The precipitation of the polysulphide sulphur is therefore not interfered with by the addition of lead arsenate nor by the simultaneous addition of either casein or gelatine. It may therefore be inferred that by such additions the fungicidal value of the lime

sulphur is not reduced but is enhanced by virtue of the increased amount of soluble arsenic. This improvement has also been observed in practice (4).

It is difficult to foretell the influence of the combination of the two components upon their insecticidal value. The considerations already put forward upon the laboratory investigation of the relative worth of the arsenicals as insecticides (p. 164) apply here and it would appear that at present there is no alternative to actual field trials.

The liability to arsenical injury has been shown to be related to the ease of formation of soluble arsenic, and upon this basis it is probable that the addition to lead arsenate of lime sulphur increases the likelihood of spray injury. Whether or not sufficient soluble arsenic will be formed to cause severe injury appears to be dependent on the climatic conditions, the variety and vigour of the tree sprayed and the type of lead arsenate used. In general the finer the particle size of the lead arsenate, the greater the amount of soluble arsenic produced, for the surface area of lead arsenate exposed to the reaction increases with the degree of fineness. It may therefore be necessary to recommend only grades of lead arsenate of not more than 300 mesh fineness (5), for the advantages of a fine state of subdivision are lost through the aggregation of the particles by the lead sulphide formed. The conclusions of Goodwin and Martin on the chemistry of the lime sulphur-lead arsenate spray have been confirmed by Hodgkiss, Frear and Worthley (6).

Experiments are in progress upon possible methods whereby the interaction may be prevented. As hydrogen sulphide is the primary reactant, the preliminary precipitation of the polysulphides in a form such that hydrogen sulphide is no longer evolved, should prevent the formation of soluble arsenic. Kearns, Marsh and Martin (7) have employed ferrous sulphate for this purpose and have shown that the production of soluble arsenic is thereby inhibited. In addition to its action as a corrective for arsenical injury, ferrous sulphate reduces lime sulphur damage, a purpose for which it is already widely used (see p. 118). Further, in view of the value of the ferrous sulphide formed as a " marker " and, possibly, as a fungicide, the ferrous sulphate-lime sulphur-lead arsenate combined wash would seem of promise though, as has been pointed out, further experience of the properties of the spray is necessary before it can be recommended.

The successful combination of direct fungicides or contact insecti-

cides with protective fungicides or stomach poisons, such as is required for the simultaneous control of Apple Scab and Apple Saw-fly (*Hoplocampa testudinea*) or for Hop Downy Mildew (*Pseudoperonospora humuli*) and Hop Aphis (*Phorodon humuli*), is dependent upon the solution of the problem of applying the protectant as a drenching wash without loss of fungicidal efficiency or increase in phytocidal properties. This problem is part of the general problem of spray retention which has already been discussed in Chapter V. The application of new knowledge of the effect of the physico-chemical properties of the spray in initial retention and tenacity to the formulation of combined washes of this type was discussed by Kearns and Martin (8).

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SPRAY RESIDUE

The widespread use, in horticulture, of general poisons such as nicotine, and the arsenic and copper compounds, has naturally aroused public anxiety through the possibilities of accidental poisoning. Different countries have resorted to legislation or have adopted recommendations to safeguard against such accidents. The general principles underlying such actions have been reviewed by Martin (1). One of the main objects is to prevent the consumption, by man or by stock, of food contaminated with poisonous spray residue.

Risk to Human Beings. In the early days of the use of Bordeaux mixture a vast amount of work was carried out on the amount of copper present in wine prepared from the sprayed grapes. In many districts it had been found necessary to apply Bordeaux mixture at intervals up to within a fortnight of the vintage, but

even then the small amount of copper retained on the grape skin which had been carried into the vat was found to be almost totally precipitated during the fermentation processes (2). The results of experiments in America on the amount of copper present on the sprayed grapes were summarized by Galloway (3) thus : " It is known that in the daily consumption of food we absorb as much if not more copper than is found on a larger quantity of properly sprayed grapes than could possibly be eaten at one time by a single individual." For the control of Blister Blight of Tea (*Exobasidium vexans* Mass.) a late application of Bordeaux mixture was found necessary. Annett and Kar (4) found the copper content of tea prepared from the plot sprayed nine days before picking approximately five times that of the tea from the unsprayed control plot. It was found, however, that even after drinking eight cups (about 2 litres) of the contaminated tea an almost inappreciable amount of copper would be consumed.

The question of arsenical residues has become of importance in many apple-growing districts since the arsenicals have been found the most practical means of controlling the second generation of the Codling Moth. Given suitable climatic conditions the larval stage of this moth is sufficiently short to permit the appearance of a second series of brood moths, which render necessary the application to the fruit of lead arsenate or some related spray even twelve to fourteen weeks after the blossoming stage.

Actually it is found that even on apples so sprayed the amount of arsenic retained is rarely sufficient to prove serious. Of a number of samples examined by the Government Analyst (5) only one contained more than 1/100th grain of arsenic per pound, the limit of tolerance suggested by the Royal Commission on Arsenical Poisoning in 1903. Of such apples about two and one half pounds, including peel, stalk and calyx, would have to be eaten to consume the maximum pharmacopœial dose. From the public health point of view, the avoidable presence of any poison in whatever amount in foodstuffs is objectionable. The regular ingestion of minute traces of lead, for example, may ultimately cause severe symptoms of lead poisoning. The removal of spray residue is therefore an essential procedure in semi-arid fruit-growing districts where conditions necessitate the late application of lead arsenate.

Mechanical methods of spray residue removal involving dry wiping or brushing of the fruit have been found unsatisfactory, for not only are they ineffective in removing the spray residue,

but the keeping qualities of the fruit, especially of pears, are impaired. The brushes have frequently to be cleaned to avoid the spread of storage rots and the wiped apples show a greater loss of weight and earlier signs of breakdown than the untreated fruit. Of the chemicals used to dissolve the spray residue the most successful has been hydrochloric acid, the concentration employed being dependent on the temperature of the solution (6). The use of copious amounts of rinse water is necessary to avoid fruit damage which develops on storage. This damage appears to be associated with the formation of soluble arsenic (7) and may therefore be avoided by the addition of lime to the rinse water. The addition of textile wetting-out agents and detergents stable to lime was recommended by McLean and Weber (8), Robinson and Hatch (9) and by Pentzer (10), particularly for heavily sprayed and waxy fruit. On account of excessive foaming, the addition of an anti-foaming agent is then required. Alternatively, a kerosene-kaolin emulsion has been suggested (11) for acid washes. Sodium hydroxide and other alkaline solutions have been employed for residue removal but have been shown to affect keeping qualities, apparently by the removal of the waxy coating of the fruit.

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Risk to Animals. The risk of injury to live stock pastured in sprayed orchards has, in general, been shown to be slight. Experiments in England (12) showed that sheep could be fed upon grass beneath trees sprayed with Paris Green without serious consequences, even though the grass itself was sprayed. O'Kane, Hadley and Osgood (13) found that sheep could be pastured on grass sprayed with lead arsenate paste at a strength of 6 lb. per 100

gallons without ill effects, though under the same conditions healthy calves exhibited some symptoms of poisoning. Poultry were found to be less susceptible and there appeared to be little danger of poisoning to chickens running in sprayed orchards.

The possibility that bees (14) may be injured by arsenic on the blossom is obviated by the simple precaution of not spraying while the flowers are open. Not only are the bees of value to the fruit-grower, but as the delicate parts of the flower concerned in the fertilization may be easily damaged by the arsenic- or copper-containing spray, the use of such sprays at this period is dangerous. The problem is not solved so easily in districts where the dusting of arsenicals by aeroplane is practised. Beekeepers in the forest areas of Germany (15) and in California (16) have suffered severe losses since the introduction of this method which can be countered by removing the bees from the area at and for a period after dusting or by the substitution of specific insecticides non-toxic to bees (e.g. quassia) for the arsenical.

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PLANT INJECTION

Apart from the question of the injection, into the plant, of toxins and anti-bodies to which reference has already been made (p. 27), many experiments have been carried out in attempts either to render the plant more resistant to attack or to kill the pest within the plant tissue by the injection of chemicals. The obstacle to success in such chemotherapeutic methods, as with serological methods, is the absence, in the plant, of a circulatory system analogous to the blood-stream of animals. It was usually sug-gested that the injected chemical would remain localized near the point of injection. For example, the claim that treatment with ferrous sulphate is a cure of Silver Leaf of Plums, etc., due to *Stereum purpureum*, was investigated by Brooks (1) not only by liberal dressings of ferrous sulphate to the roots but also by its injection into the diseased tree. Brooks and Bailey (2) were unable to

report that the method was successful and were of the opinion that the fungus would be killed only within a limited zone.

The rules underlying the distribution of an injected substance in woody plants were investigated by Roach (3). He showed that the injected liquid followed the direction óf the vascular strands and that, by the proper distribution of the injection holes, a complete permeation of the tree could be obtained. Roach recorded the results of four trials of the control of Apple Powdery Mildew, *Podosphœra leucotricha* (Ell. & Ev.) Salm., by the injection of sodium thiosulphate solutions. Two of the trials were successful and two failed, an indication that some condition necessary for success had not been recognized.

Attempts to apply plant injection methods to the control of insect pests have been conducted with the view of rendering the plant sap distasteful rather than poisonous to the insect—a deterrent rather than an insecticidal action. Against Woolly Aphis (*Eriosoma lanigera*), Dementiev (4) reported that the injection of barium chloride (1 : 350) into an infested tree caused the disappearance of the aphides within ten days. Müller (5) obtained similar results by the injection of pyridine and of aluminium sulphate.

An interesting suggestion was put forward by Andrews (6), who observed that the extent of infestation of tea bushes by Mosquito Blight (*Helopeltis theivora*) appeared to be related to the potash/phosphate ratio of the nutrient supply. He reported that, after a direct injection of solutions of potassium salts, heavily infested bushes quickly became free from the pest without any deleterous action upon the plant.

The poisoning of the pest by the injection into the host of potassium cyanide was found possible by Sanford (7) against Fluted Scale (*Icerya purchasi*) on Spanish Broom, peach and orange. His results were confirmed by Shattuck (8), who successfully controlled boring insects on elms and Black-locust trees by this means. Moore and Ruggles (9), however, have questioned the value of hydrocyanic acid when used in this manner. They found that the gas was confined to the older tracheæ which, in woody trees, are dead and therefore uninjured. As the boring insects live in the cambium they would remain unaffected unless the gas penetrated into this living part óf the tree. Such a process they considered, though perhaps possible in herbaceous or semi-wooded plants, would endanger the host.

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CHAPTER X

WEED KILLERS

If dirt may be defined as " matter in the wrong place," weeds would become " plants in the wrong place." Attention will be given not so much to the control of weeds growing merely as a nuisance, as upon paths, etc., but weeds actually growing as a pest among the crop. In the former case it is possible to apply chemicals toxic to all vegetation, but in the latter case it is necessary to apply measures which will not cause undue injury to the crop plant. There are, however, occasions when the defoliation of a crop plant may be required. The destruction of potato haulm infected with blight, *Phytophthora infestans*, was reported by Small (1) and by Bates and Martin (2) to reduce tuber infection.

The main ill effects of weeds on the crop are due to competition for the available food and water supply of the soil. As a result of this competition, it has been stated (3) that, in the United States, the yield of corn is reduced by 10 per cent. by the presence of weeds. A further injurious feature of weeds was suggested by Pickering (4), who, from the results of experiments upon the effect of grass upon fruit trees, advanced the view that the plant produces, in the soil, toxins which affect the growth of adjacent plants. Such a theory might provide a factor in the determination of ecological plant associations and would also explain the bad effects of certain weeds on crops. Brenchley (5) was, however, unable to deduce evidence of the excretion of toxic material from the roots of plants.

Further reasons for weed control are that certain weeds may provide a host plant for pests, that the weeds may be poisonous or noxious to human beings and cattle : for example, the presence, in cereal crops, of Corn Cockle (*Agrostemma githago*), which contains a poisonous glucoside and imparts injurious properties to the flour ; the wild onion (*Allium* spp.) is reported to give a disagreeable flavour to the milk of cows feeding upon an infested pasture.

The normally evolved systems of cultivation are usually sufficient

to suppress weed growth. Crop rotation, where possible, is of primary importance, and with root crops hoeing is a standard measure. Again with weeds which are propagated solely by seed, the reaping of the crop prior to the ripening of the weed is a commonly and automatically applied weed-control measure. There are, however, certain cases where such cultural means of control are inapplicable or where, owing to the ripening of the weed before the harvesting of the crop, they are ineffective, a widespread example being the presence of charlock (*Brassica sinapis*) among cereal crops.

Advantage may be taken in such cases of the selective action of certain chemicals which are found to affect the weed more seriously than the crop. This selective action appears to have been first noticed by a French vine-grower, L. Bonnet, who, in 1897, observed that the leaves of charlock were blackened and killed by copper sulphate, whereas the grass was unaffected. The following-up of this chance discovery has resulted in a number of such weed killers being employed, more particularly for the weeds of cereal crops under circumstances in which the cultural methods cannot be used.

The weed killers of this type which have found widespread practical use may all be classed into one group.

THE SULPHATE GROUP

Copper Sulphate. Copper sulphate, employed by Bonnet, has been used in many countries, especially England, against charlock. It is applied in solution, the requisite dosage and strength varying with the climatic conditions of the locality (6).

The action of copper sulphate upon the plant appears to be related to the amount of spray retained upon the plant's foliage. The leaves of cereals are thin and narrow and, being of an erect habit, the spray readily runs off: moreover, they are usually covered with a dense mass of fine hairs or with a " bloom " difficult to wet, whilst it is possible that a more resistant nature of the cuticle plays some part. The leaves of charlock and other weeds, by virtue of their more horizontal spread, retain the spray, are more easily wetted and are perhaps more sensitive to the toxic material of the spray.

The application of copper sulphate to the soil is generally without serious interference with subsequent plant growth, for the copper is rapidly adsorbed by the soil and will, unless with abnormal soil or

with the use of large amounts, fail to reach the plant's roots or to bring about any marked change of soil properties.

Ferrous Sulphate. Ferrous sulphate was one of the weed killers with which Bolley (7) obtained excellent results and is still one of the most popular weed killers in America. It has been used more frequently in solution but may also be employed in powder form. Stronger solutions are used than with copper sulphate, but it is cheaper, though less convenient to work with, for it rapidly oxidizes.

The toxic action of ferrous sulphate was considered by Olive (8) to be due to its osmotic properties rather than to an absorption by the leaf. The dried salt was thought to cause a plasmolysis of the leaf cells, though Schultz (9) showed the leaves to be unharmed after being plasmolysed by various salt solutions for several hours if the salt be then washed off. The blackening of the plant tissue caused by the application of the ferrous sulphate Olive considered to be due to the formation of the sulphide, Schultz to the reaction of the iron and the tannic acids of the tissue. Åslander (10) concluded that the toxic action of ferrous sulphate is not due essentially to plasmolysis but that absorption and a chemical action of the spray does occur. He found that the strength of the action was dependent upon the weather, a dry calm sunshiny day with a high relative humidity giving the best results.

Kainit. This, originally a crude product of the Stassfürt deposits, is the familiar potassic fertilizer. The mineral " Kainite " is represented by the formula $KCl.MgSO_4.3H_2O$, but the manurial " Kainit " generally contains varying proportions of sodium and chlorine. Although the general statement that it contains sulphate of potash is probably not correct, Kainit is classed under the sulphate group, for much sulphate in the form of magnesium sulphate is present.

Kainit is generally applied as a fine dust, whilst dew is still on the plants. Its action is usually held to be plasmolytic, the fine dust being retained in greater amount upon the hairy horizontal leaves of the weed. In addition to its selective action upon weeds, Kainit contains potash, the manurial value of which compensates in part for the cost of the treatment.

Ammonium Sulphate. The application of ammonium sulphate has long been known to affect the botanical composition of herbage and its main present use, frequently admixed with calcined ferrous sulphate, is as a lawn dressing. Its use as a selective weed killer may be illustrated by the work of Garrad (11), who found

its rapid action of use in the control of Thanet Weed (*Lepidium draba* L.). The effects of ammonium sulphate upon turf composition are described by Blackman (12), who showed that the previously-held view that its activity was associated with its action in increasing soil acidity is untenable. He suggested a specific toxic effect of the ammonium ion, perhaps related to the combination of the ion with carbohydrates or with organic acids. Upon this hypothesis, susceptible plants, i.e. weeds, should show a low content of available carbohydrate and/or organic acids whereas resistant plants, i.e. grasses, should have a high content of these substances.

Sulphuric Acid. This acid was first recommended by Woods and Bartlett (13) and has found the greatest practical usage, despite the difficulties of application, in France. Rabaté (14) found it, at dilutions of 5–15 per cent. H_2SO_4, more active than powdered ferrous sulphate and not causing the partial poisoning of the cereal and decrease of straw growth which he observed with copper sulphate, sodium chlorate and various other chemicals.

He found the acid to act more strongly upon the younger and more turgid foliage and concluded that it plays the part of a dehydrating agent. Åslander, on the other hand, concluded that the high hydrogen ion concentration of the acid is responsible for the toxic action, but showed that the plant is able to absorb and so neutralize the action of some of the acid. The plant was killed only when this protective capacity of the plant was exceeded, a protective capacity he found dependent upon the thickness and modifications of the outer epidermis.

Rabaté claimed that the sulphuric acid spray also acts against certain of the soil organisms responsible for disease of the cereal stalk, notably *Leptosphœria herpotrichoides* de Not. and *Ophiobolus graminis,* both fungi which are reported to be sensitive to acidity. The effect of the application of sulphuric acid does not appear to be unduly serious and Rabaté pointed out that, if applied in equivalent amount, sulphate of ammonia would decalcify the soil to the same degree as sulphuric acid.

The rapid action of sulphuric acid on foliage is of special use in the destruction of haulm infected with Potato Blight (*Phytophthora infestans*) (2, 15). If the crop is lifted before the haulm has been completely killed by the disease, infection of the tubers may occur, to prevent which the diseased haulm is killed by spraying with dilute (10–12 per cent.) B.O.V. (Brown Oil of Vitriol, 77 per cent. by wt. H_2SO_4).

The peculiar virtues of the metallic sulphates as selective weed killers reappear in their value for the destruction of slugs, molluscs of the order Limacidæ. The use of substances which apparently act as mechanical barriers over which the slug is unwilling or unable to pass, is the more usual method employed as a preventive against these pests, but there are available materials directly toxic to the slug. Anderson and Taylor (16) recommended a direct application of copper sulphate which they found unique in its toxic action on the pest. They proposed the use of a mixture of copper sulphate and kainit applied by means of a manure distributor.

The sulphates are likely to be displaced, as slug killers, by metaldehyde, reports of the success of which were confirmed by Gimingham and Newton (17). Metaldehyde is a polymerized acetaldehyde, marketed under the proprietary name " Meta " for use, in tablet form, as a solid fuel to replace the spirit lamp. It was perhaps due to the chance loss of a tablet by a picnic party that its effect on slugs was first observed. Jary and Austin (18) suggested that the action of " Meta " prevents the slugs from regaining natural shelter during daylight. Exposed to sun and partially desiccated by slime exudation, they die within a day or two.

THE CHLORATE GROUP

For the destruction of perennial weeds on arable land, the use of a weed killer toxic to deep-rooted plants is necessary. Of such materials, the water-soluble chlorates have been found of particular value, their first recorded use being, in 1901, upon prickly pear (*Opuntia* sp.) in Australia (19). The high toxicity of sodium and potassium chlorates to plants has been attributed to a rapid absorption by the foliage and translocation thence to the roots via the vascular system and to their rapid penetration into the soil where their decomposition is slow. Åslander (20) found that the rate of penetration of soil by the chlorates was greater than that of sodium thiocyanate and of sodium cyanide, both of which are rapidly decomposed, and of sodium arsenite.

The physiological action of the chlorate ion has been examined by Neller (21), who ascribed toxicity to an inhibition of enzymatic activity. He suggested that the slow decomposition of the chlorate with the formation of nascent oxygen was associated with a marked reduction of catalase activity in the poisoned plant.

The use of chlorates as selective weed killers and, indeed, their

use on all ground except that which is to be kept free of vegetation, has been threatened by their marked residual effect. Owen (22) recorded many cases of damage to plants adjacent to paths treated with chlorate weed-killers and to plants in pots " stood-out " on chlorate-treated ground. The similarity of the symptoms of chlorate-poisoning and of certain virus diseases is noteworthy. In regions of low rainfall, continuous leaching with irrigation water was found by Crafts (23) to be the best way of removing residual chlorate.

Another disadvantage of chlorates is the high inflammability of organic matter in contact with chlorates. The dangers attendant upon the drying of clothes wetted with chlorate spray are well portrayed by Ashton and Bruce (24).

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CHAPTER XI

FUMIGANTS

Fumigation may be regarded as the employment of the toxic chemical in a volatile form. To avoid wastage, the method is only applicable for the treatment of an enclosed space such as the glasshouse.

The principle of fumigation is undoubtedly of great antiquity; the burning of aromatic herbs, of resins and of incense, though probably of little real effect upon micro-organisms, was perhaps adopted as a preventive against disease. At least, the strong odour would effectively mask the smell of putrefaction which was considered the cause of disease. Originally applied for the treatment of houses, the method has since been extended for use against certain glasshouse pests and for the treatment of orchard trees.

For the latter purpose, the tree is covered by an air-tight tent into which is introduced the requisite amount of fumigant. After exposure for the necessary time, the tent is removed and re-erected over the next tree. The material of the tent must be light for easy manipulation, must be pliable to lie close to the ground, of sufficient strength to prevent tearing and as gas-tight as possible. A tightly woven cotton drill is generally employed which may be proofed with certain varnishes or oils (1).

The fumigant should have, apart from its toxic properties and non-injuriousness to the plant, a ready volatility, good powers of diffusion and should be cheap; qualities possessed in good measure by the more important of the fumigants, e.g.

Hydrocyanic Acid. Hydrocyanic acid was first employed by D. W. Coquillett (2), in 1886, against the Scale insect pests of citrus in California. He introduced the method more particularly against the Cottony Cushion Scale (*Icerya purchasi*), then a serious menace to citrus-growers. With improvements in technique and in the preparation of the gas, the method has now become an important routine not only in general glasshouse cultivation but also in the

more specialized case of citrus culture against those scale insects which are highly resistant to other insecticides.

Hydrocyanic acid is conveniently generated by the action of an acid upon a cyanide, the first materials employed by Coquillett being potassium cyanide and sulphuric acid. As the amount of fumigant used has to be carefully controlled, the two materials should be mixed in the correct amount and the quantity of water present must be regulated. The potassium cyanide should be of not less than 93 per cent. purity (3) and the acid of sp. gr. 1·84. The acid should not be diluted to an extent sufficient to prevent the complete evolution of the hydrocyanic acid which is readily soluble in excess of water. Yet enough water should be added to prevent secondary reactions by which the hydrocyanic acid is decomposed and to prevent the separation of solid potassium sulphate, which might include some of the cyanide preventing its complete decomposition—this solidification of the reacting mixture is known popularly as " freezing."

The typical formula is 1–1–3 ; i.e. one ounce 98 per cent. potassium cyanide added to one fluid ounce of strong acid diluted with three fluid ounces of water. The cyanide should be added to the diluted acid to prevent a polymerization of part of the cyanide compounds.

The more expensive potassium cyanide was later replaced by sodium cyanide, used in a similar manner. As high-grade (97 per cent. purity) sodium cyanide liberates a greater relative amount of hydrocyanic acid than potassium cyanide, the proportions of sodium cyanide, sulphuric acid and water usually employed are 1–1½–2 to 1–1½–3. The 97–98 per cent. sodium cyanide is, by virtue of this higher proportion of cyanide, sometimes described in terms of potassium cyanide as of 129–130 per cent. cyanide.

Although with cautious management there is ample time for the operator to move away to safety after dropping the loose cyanide into the prepared " pots " of acid, there have appeared on the marked " Safety Cyanide Packages " obviating danger (4). These packages are of metal with thin zinc foil sides containing weighed amounts of sodium cyanide. The acid first dissolves away the zinc before coming into contact with the cyanide. Careful standardization of the amount of zinc used is necessary and allowances must be made for the extra amount of sulphuric acid neutralized by this reaction and for the water required for the solution of the zinc sulphate formed.

The ready liquefaction of hydrocyanic acid at 26·5° C. led to the suggestion by Mally (5) in 1915, of the use of liquid hydrocyanic acid for fumigation purposes. The anhydrous liquid may be pumped into the enclosed space, enabling an easier and more rapid application and, since it is introduced as a fine spray, a more thorough distribution of the gas. Further, as Mally pointed out, in the preparation of the hydrocyanic acid by the use of sulphuric acid there is a danger of the burning of the fabric of the tent by the acid carried up by the gas, a risk obviated by the use of liquid hydrocyanic acid. This method became widely recommended in the United States and the technique of the process was worked out by Quayle (6) and by Woglum (7).

A more convenient method is the use of solids, such as calcium cyanide, which are decomposed by moisture to liberate hydrogen cyanide. Calcium cyanide is made by the " Cyanogas " process, which is the fusion of salt with calcium cyanamide, or by the combination of liquid hydrogen cyanide with calcium carbide ("Citrofume," 8). According to Metzger (9) the latter reaction yields a product of composition more akin to the acid cyanide, $CaH_2(CN)_4$ than to the normal cyanide $Ca(CN)_2$. In the presence of atmospheric moisture, these products decompose to form calcium hydroxide and hydrocyanic acid. Their application therefore merely involves the discharge of the requisite amount of the dust into the enclosed space containing air of a sufficient humidity to permit its decomposition. The first trials with calcium cyanide were reported in 1923 by Quayle (10) for tent fumigation, and the method has since been extended to glasshouse work with excellent results (11). The relationships between humidity and the decomposition of calcium cyanide dusts were examined by Quayle (12).

Other dust products which evolve hydrocyanic acid gas when exposed to moisture are the sodium cyanide-anhydrous magnesium sulphate mixture used by Ladell (13) and the bicarbonate-cyanide mixture devised by Speyer and Owen (14). Three parts by weight of sodium bicarbonate and one part of sodium cyanide (98 per cent.) are thoroughly mixed and the required amount is distributed along the paths of the glasshouse.

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Action upon the Insect.   The mode of action of hydrogen cyanide upon organisms, both plant and animal, has been the subject of much discussion.   The action would appear to be an interference with the normal enzymatic activity, probably an inhibitory action upon tissue oxidation, by a combination with the catalysts present in living tissue.   Outside the body, Loevenhart and Kastle (15) and Böck (16) observed the " poisoning " effect of the acid upon the influence of those finely-divided catalysts, such as colloidal platinum, called " inorganic ferments " by Bredig.   Warburg (17), who investigated the effect of hydrogen cyanide upon the fermentation processes of yeasts, attributed the reduction of activity to a combination of the cyanide with the iron present, a metal known to play an important rôle as a catalyst in fermentation.   Voegtlin, Johnson and Dyer (18) considered that the cyanide does not act specifically upon the iron of the plasma but rather that it disturbs the equilibrium of the sulphur compounds.   They adduced evidence that, *in vitro*, certain sulphur groups are reduced by the action of the hydrogen cyanide, in connection with which the detoxicating effect of various sulphur compounds on cyanide poisoning is of interest (19).

For the action of hydrogen cyanide upon insects, Shafer (20) regarded its disturbance of the normal balance of the reductases, catalase and oxidases as the possible determining factor in causing death.   Haas (21) made the suggestion, of interest in connection with the effect of copper sprays upon the phytocidal activity of hydrogen cyanide, that scale insects resistant to cyanide fumigation contain less copper than sysceptible scale insects.   He considered that the effect of copper was to enhance the toxic properties of hydrogen cyanide.

For practical purposes, in order to avoid injury to the plant, it is necessary to regulate the amount of the fumigant employed.   The

" dosage " required to kill any particular insect species is dependent, among other factors, upon the time the insect is exposed to the hydrocyanic acid. Quayle and Knight (22) found that, at any definite temperature, the time required for a 100 per cent. kill is inversely proportional to the dosage. This relationship becomes of importance in tent fumigation where the time taken for the treatment is of economic value. The dosage required is dependent, moreover, upon the type of insect. Knight (23) showed that the effect of temperature on the relative resistance of insects to hydrogen cyanide differs according to species. The percentage kill of the Coccinellid beetle *Hippodamia convergens* Guér., was greatly reduced, at a definite dosage and time of exposure, by a fall of temperature, which renders the beetle less active. With the Red Scale (*Aonidiella aurantii*), however, the percentage kill under standard conditions of fumigation was not greatly affected by change of temperature, within the limits of safety to the tree. Nor is the activity of this insect greatly affected by change of temperature. Knight therefore recommended that against this pest, fumigation should be carried out when the trees are partially dormant and less liable to injury by higher dosages.

In California it was found that the effectiveness of the standard fumigation methods suffered as there developed strains of the scale insects of increased resistance to the poison. Quayle (24) reported, in 1922, that in at least two localities in California, the Red Scale had become so resistant that the dosages of hydrocyanic acid found, in earlier fumigation practice, to be fatal were tolerated. The increased dosage necessary for a satisfactory kill had become too great for the safety of the tree. This development (25) confirmed by Woglum (26), may have been due to the selective breeding of resistant strains, an hypothesis verified by Boyce (27) and by Gough (28) who showed that resistance to hydrogen cyanide is an hereditary property.

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Action on the Plant. Hydrocyanic acid is, under certain con-
ditions, toxic to plant growth, but de Ong (29) showed the existence
of a considerable margin of safety between the killing strength
necessary for an insect such as Phylloxera and that causing injury
to the more hardy plants. Owing to the differences in the suscepti-
bility of different species, there do exist, however, certain plants
on which it is unwise to employ hydrocyanic acid as a fumigant.
Weigel (30) mentioned among the ornamental greenhouse plants,
in particular the sweet pea, the chrysanthemum and the rose.

The injurious action of hydrocyanic acid upon the plant foliage
proved the most severe difficulty encountered in the early days of
cyanide fumigation. Coquillett succeeded in reducing the injury
by permitting only a slow evolution of the gas, whilst F. W. Morse
(31) introduced the " soda " process in which sodium bicarbonate
was mixed with the cyanide, the hydrocyanic acid thereby being
diluted by the carbon dioxide simultaneously evolved. Later,
however, Coquillett found that the extent of the foliage injury was
dependent upon the moisture present and the action of sunlight
during fumigation. This latter factor he demonstrated by the less
injury occasioned by fumigation in the dark.

Quayle (32) suggested that the lessened danger of plant injury in
night fumigation was due to the differences of light, temperature and
moisture affecting the stomatal opening and the chemical relations
governing gas absorption and cuticular defence. Clayton (33) found
that the conditions which bring about an opening of the stomata
were those under which the injury was most severe. Further, he
showed a positive correlation of the sugar content of the plant tissue
with resistance to the toxic effects of hydrocyanic acid. The lower
the temperature, the less active the plant and the less the injury
caused by hydrocyanic acid. Further, Woglum (34) found that
injury to the plant is increased by exposure to sunshine, both
immediately before and after treatment, and by sudden changes
of temperature during fumigation.

It was at one time thought that the hydrochloric acid generated
from chloride impurities of the commercial cyanide was responsible
for the injury (35). Moore and Willaman (36), however, established

the injurious nature of hydrocyanic acid and examined its mode of action upon the plant tissue. They found that the plants exposed to the acid absorbed more or less of the gas, the immediate effect of which is a reduction in respiration due to a disturbance of the activity of the oxidases and catalase, an action already noted in the action of the acid upon insects. Shill (37) was unable to confirm this conclusion with citrus for he showed that the hydrocyanic acid treatment led to an increase in respiration which returned to normal some thirty-five hours after fumigation. Moore and Willaman also showed that there was an increase in the permeability of the leaf septa (presumably, the plasma-membranes) causing a less rapid intake of water from the stem and a more rapid cuticular transpiration. Thus, in mild fumigation, there was a temporary wilting of the plant.

Woglum (38), in 1918, directed attention to the greater injury caused by cyanide fumigation following the application of Bordeaux mixture. It was found also that citrus, treated with copper salts for the control of exanthema, a copper-deficiency disease, were more susceptible to hydrogen cyanide (39). Butler and Jenkins (40) ascribed the injury which follows Bordeaux spraying to the formation of a soluble and phytocidal complex copper cyanide, a conclusion confirmed by Guba and Holland (41) who regarded the cuprocyanide $CaCu_2(CN)_4,5H_2O$ or a similar soluble compound as the phytocidal material. Haas and Quayle (39) correlated the increased injury with the copper content of the plant and suggested, tentatively, that copper augments the toxic properties of hydrogen cyanide.

On the other hand, there is evidence to show that the presence of traces of hydrocyanic acid brings about a stimulation of plant growth.* Moore and Willaman found that the increase of permeability, if not too severe, was followed by a rate of growth and of fruit production in excess of the normal. Clayton found that the maximum beneficial results from stimulation occurred at a dosage of hydrocyanic acid fatal to insect life and just below that of injury to the plant. Gassner (42) utilized this stimulation of plant growth as a method of " forcing " plants by regular treatment in dilute atmospheres of hydrocyanic acid.

* This phenomenon affords an example of the Arndt-Schulz law, that small quantities of a poison act in the opposite manner to large quantities.

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Precautions in Application. The elucidation of the factors governing the toxicity of hydrocyanic acid, both to insect and to plant life, enable certain precautions to be taken to ensure a satisfactory fumigation :

(1) Calculation of the " dosage " required. This regulation requires a knowledge, not only of the degree of purity of the chemicals used, but also of the cubic capacity of the space to be fumigated. The determination of the volume of a glasshouse is usually a matter of simple arithmetic, whilst for tent fumigation, formulæ based on the resemblance of the tent to a cylinder surmounted by a hemisphere, or " dosage tables " based on the distance round the base of the tent and the longest distance over the tent, may be used. Further, to maintain the required mean concentration of the gas for the correct length of time, it is necessary to ensure, as far as possible, freedom from leaks. The fumigation is therefore best carried out in calm weather.

(2) Fumigation at night-time to lessen the risk of injury to the plant. The general recommendation is to start the treatment not before one hour after sunset. At this period the temperature is lower and less likely to fluctuate while there is less possibility that the pre-fumigation exposure to sunlight will have any injurious result.

(3) The withholding of watering for twenty-four hours before fumigation. The presence of excessive moisture, especially at the roots, predisposes the plant to injury and part of the requisite dosage of the hydrocyanic acid may be lost by solution in the water. For the latter reason, water tanks in the house should be covered.

If calcium cyanide is used as the source of hydrogen cyanide, the relative humidity of the house should be above 79 per cent.

(4) Attention to the risk to human beings and animals.

Naphthalene. This substance is obtained by crystallization from certain fractions of coal-tar distillate and is marketed in various stages of purity dependent upon the degree of separation of the carbonaceous and mother liquor impurities. The least pure form, the Undrained Salts or Unwhizzed Naphthalene, contains relatively large amounts of creosote and phenols (see p. 201). Part of the creosote is removed by allowing the " salts " to drain, a process yielding the " Drained Salts," and the mother liquor may be more thoroughly separated by pressure or by the centrifuge processes which yield the " Hot-pressed " and " Whizzed " Naphthalene. Finally, the purest commercial form, the " Pure Flake " Naphthalene is obtained from which the carbonaceous matter has been removed by sublimation.

Pure naphthalene is a white crystalline substance with a characteristic odour. The material has long been known to possess insecticidal properties and is employed, under the popular name of " Carbon " or " Camphor " balls, as a repellent for clothes moths (Tineidæ), and as a fumigant in museum cases, etc.

Many attempts have been made to extend its employment for glasshouse fumigation but only in exceptional cases has naphthalene proved a successful competitor to hydrocyanic acid. Lloyd (43) tested its efficiency against the Greenhouse White Fly (*Trialeurodes vaporariorum*). He found that its effect was due more to the presence of phenols, for the more impure samples proved the more potent in action. Speyer (44) tested naphthalene against the red spider *Tetranychus telarius*, a pest resistant to most volatile poisons. He found that above 74° F., the red spider was killed after forty hours' exposure to naphthalene vapour, and recommended for fumigation, " Pure commercial White Flake Naphthalene, Grade 16," i.e. passing a sieve of 1/16th inch mesh. The presence of much fine powder was objectionable and, contrary to Lloyd's results with the White Fly, he found that phenols did not increase the effectiveness of naphthalene against red spider, but were an undesirable impurity owing to a serious scorching action (45).

Speyer's method, although successful in cucumber houses, proved less so in tomato houses (46), one factor being that, owing to the relatively low temperature, effective fumigation cannot be completed in a single night. To shorten the time required, Parker (47) intro-

duced a vaporizing lamp. This is frequently used in carnation houses, but the control of the concentration of naphthalene vapour is not as rigid as is required to avoid injury to certain other plants. Hartzell and Wilcoxon (48) devised an apparatus whereby air, drawn from outside, was saturated with naphthalene vapour and discharged into the house. Later, with Youden (49), they adapted the method to a recirculatory process, controlling the concentration of naphthalene vapour by the use of solutions of naphthalene in inert solvents such as light lubricating (hydrocarbon) oil.

Naphthalene vapour has, under certain conditions, a pronounced scorching action upon the cucumber plant, an action which may be prevented by the presence of sufficient moisture. It would appear that the naphthalene vapour enters the plant tissue via the stomata and, being insoluble in water, the amount of naphthalene which enters is reduced if the plants are giving out and not taking in moisture. Speyer found naphthalene fumigation had no harmful action on cucumber flowers but that the fruit absorbed the vapour. Fortunately, if the fruit be exposed to fresh air after the treatment, the taste imparted to it soon disappears.

The tolerance of ornamental plants to naphthalene fumigation differs greatly (50) but the susceptible varieties and species have been tabulated in most practical hand-books (see 51).

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Tetrachlorethane. This liquid is the active agent of certain proprietary fumigants for use against the White Fly. It is produced commercially as a fat solvent, and has the advantage of non-inflammability. Chemically it is represented by $C_2H_2Cl_4$, a derivative of ethane C_2H_6 in which four of the hydrogen atoms are replaced by chlorine.

Tetrachlorethane was first used experimentally upon White Fly by Lefroy (see 52) in 1915. Lloyd (53) tested the material and

found it undoubtedly toxic to the adult fly. It appeared to kill the scale through its effect upon the waxy covering of the larval stages. The flies died in the attempt to emerge from this covering. This hypothesis is in agreement with the observation that tetrachlorethane has little effect upon aphides but that mealy bugs are affected.

Fumigation may easily be carried out by suspending sacks soaked with the required amount of the fumigant in the closed glasshouse at dusk, the temperature of the house being maintained at 65–70° F. (54).

Tetrachlorethane cannot be used in the presence of many plant species owing to its phytocidal action. Lists of plants resistant and susceptible to the fumigant are quoted by Parker (54) and by Fox Wilson (52). Speyer (55) found a remarkable difference even in the varietal susceptibilities of various ornamental plants. It was, in the case of the chrysanthemum, almost possible to tell the variety from the nature of the injury to the foliage caused by the vapour of tetrachlorethane.

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Nicotine. Nicotine is still a popular glasshouse fumigant for aphid control (56). Tobacco or some suitable nicotine-containing extract, mixed with some slow-burning material is either ignited or heated on an iron plate over a small charcoal fire or a spirit lamp. The nicotine is thereby evolved as a vapour which then acts in the same manner as nicotine from dusts and sprays applied direct to foliage.

Sulphur. The processes by which sulphur can be applied to the plant in the form of particulate sulphur have already been discussed (see p. 106).

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An important application of fumigation for plant protection purposes is for the treatment of " seed " and nursery stock. Under certain present-day legal requirements, enforced in many countries,

the importation of such plant products is permissible only after a satisfactory fumigation or sterilization. Hydrocyanic acid is the more usual fumigant employed for such purposes.

Miscellaneous Fumigants. A brief reference may be made to insecticidal fumigants which, by reason of their high phytocidal properties and other reasons, are unsuitable for use in the presence of growing plants, but which may be safe for use in empty glasshouse or infested stores. The literature of the control of pests of stored products contains valuable studies of the factors of chemical structure and of insect physiology influencing toxic action, studies which deserve application to plant protection and which may reveal useful plant fumigants.

The pioneer work of Moore (57) indicated a correlation between volatility and toxicity over a wide range of organic compounds, a discovery extended by Ferguson (58) to the action of the chlorinated ethylenes on the grain weevil *Sitophilus granarius* L. A comprehensive search for stored produce fumigants undertaken by Neifert and his colleagues (59) led to the introduction of a mixture of ethyl acetate (40 volumes) and carbon tetrachloride (60 volumes). The addition of carbon tetrachloride, which was necessary to lower the inflammability of the ethyl acetate vapour, reduced the already low toxicity of the latter. Roark and Cotton (60) therefore examined a wider range of aliphatic compounds, reviewing their results in relation to chemical structure. The most promising of the compounds tested were ethylene dichloride, ethylene oxide, certain alkyl formates and esters of the halogenated fatty acids. The halogen- and sulphur-substituted organic compounds were also surveyed by Shepard, Lindgren and Thomas (61). Of the physiological studies, mention may be made of Busvine's (62) investigations of the insecticidal action of ethylene oxide.

The practical application of these investigations is foreshadowed in the use of **benzene, C_6H_6,** as a fumigant for the control of Blue Mould of tobacco (*Peronospora tabacina* Adam.) introduced by Angell, Hill and Allan (63) in Australia and developed by Wolf and his co-workers (64) in the U.S.A. Clayton (65) reported the successful substitution for benzene of *p*-**pdichlorbenzene** for the control of this disease. Another chlorinated derivative, *β.β'*-**dichlorodiethyl ether,** $(ClC_2H_4)_2O$ was proved suitable as a plant fumigant in preliminary trials by Wilcoxon and Hartzell (66). The action of the aliphatic alcohols and the corresponding formates upon Red Spider was determined by Read (67), who observed an

increase in toxicity as the series was ascended, methyl formate being exceptionally toxic.

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SEED TREATMENT

To ensure the continuation of the species, it is necessary that the pest, during the absence or dormancy of its host, should itself either pass into a resting stage or find an alternate host. For example, the pest may be attached, in a like dormant condition, on or within the seed of its host. The term " seed " is here used in its widest sense to embrace fruit, tuber, bulb, true seed, or other form in which the plant overwinters and which is sown or planted by man to yield the crop. It is during this stage of seed transmission that the pest is attacked in seed disinfection. Alternatively, it may be possible by treatment of the seed to protect either the seed or seedling from attack by soil-borne fungi, a principle termed seed protection.

The various methods of seed treatment employed fall conveniently under the three heads : (i) Mechanical ; (ii) Chemical ; (iii) Physical.

MECHANICAL METHODS

Such methods are only available when the presence of the resting stage of the pest causes some abnormality in size, weight or appearance, by which it is possible to separate the good from the bad seed. Among such methods is to be included the careful examination of seed samples and a discarding of those samples which show an abundance of weed seeds. A satisfactory removal of weed seeds and cleaning of seed is now enforced in England under the Seeds Act of 1920, by which Seed Merchants are required to make a declaration as to the purity and percentage of germination of certain agricultural seeds.

A frequent source of trouble is seed of Dodder (*Cuscuta* spp.) parasitic plants, in seeds of the clover group. Screening and sieving may not give complete separation and there have been several ingenious suggestions, such as the Dossier machine with velvet linings on which the rougher coated dodder seeds are retained.

More recently, Foy (1) employed a magnetic device in which the rough-coated dodder in the impure seed, when mixed with a powder containing iron remains covered, and is therefore removed by passing under a magnet. The pure clover seed is then re-cleaned by passing through a polisher.

An ingenious demonstration, due to von Degen, was recorded by Saunders (2) in which advantage is taken of the difference in elasticity of the seed coats of dodder and clover. If red clover and dodder seeds are dropped from a height of about eighteen inches into an ordinary saucer, the clover seeds bounce out of the saucer while the dodder seeds remain.

The elimination by seedsmen of misshapen and damaged beans and peas goes far to remove those infected with various fungus and bacterial diseases, e.g. *Mycosphærella pinodes* (Berk. and Blox.) Stone, *Ascochyta pisi* Lib., *Bacterium medicaginis* var. *phaseolicola* Burk (3).

Hennig (4) proposed an interesting method for the mechanical treatment of the Loose Smut of Barley (*Ustilago nuda*). With the two-rowed barleys of the nodding type, *Hordeum distichum nutans*, only those flowers at the apex and base of the ear usually open during fertilization. It is at this stage that infection occurs and the closed cleistogamous flowers of the middle of the ear may escape. As the flowers at the base and apex of the ear yield smaller grain, Hennig concluded and showed that the small grain bears a higher infection than the larger grain from the middle of the ear. Sifting to remove the smaller grain was also found to give partial control of the Stripe Disease of Barley (*Helminthosporium gramineum* Rabenk.) and there were indications that oats from small seed were more liable to attack by Stem Rust (*Puccinia graminis*).

In the " Purples " Disease of Wheat, caused by the nematode *Anguillulina tritici* (Steinb.) Gerv. and v. Ben., the normal wheat grain is replaced by a gall enclosing numerous larvæ. These galls are not unlike the normal grain in appearance but have a lower specific gravity and can therefore be separated by flotation in a 20 per cent. sodium chloride solution. The good grain is rinsed in clean water and, to prevent ill effects to the germination, Leukel (5) recommended sowing immediately after rinsing. Chester (6) suggested the flotation of delinted cotton seed in water, for he found that the fraction sinking gave a germination and emergence twice as good as that of the lighter seed.

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CHEMICAL METHODS

The practice of steeping seed in liquids such as wine or urine was employed from the earliest times, though perhaps more for the purpose of destroying the insect pests present. In the seventeenth century, in England, as a preventive against " smuttiness " of wheat, it was usual to " brine " the seed corn. Tull (7) in 1733, recorded how, some seventy years previously, a ship laden with corn had gone ashore near Bristol. The grain was too saturated with sea water to be used for milling purposes, but local farmers sowed some of the salvaged wheat. It was observed that the crop produced was free from smut, in strong contrast to that of neighbouring fields sown with normal wheat. Even in 1733, however, it was found that sodium chloride gave but an incomplete control of the disease, for Tull himself had the suspicion that the " drowned " wheat at Bristol, being foreign, might have originally been free from smut and " might not have been smutty the next year though it had not been soaked in sea water." A further stage of the development of chemical seed treatment occurred in 1761, when Schulthuss (8) suggested the use of copper sulphate in place of salt.

The scientific foundations of chemical seed disinfection were laid by Prévost (9), who, in 1807, discovered the nature of the " smut " disease, against which copper sulphate had been used with success. He observed the germination of the smut spores in water and the prevention of this germination by the presence of a trace of copper sulphate. His work was repeated and extended by Kühn (10), who, in 1859, popularized the copper sulphate treatment of cereal grain by his extensive experiments.

An interesting modification of the copper sulphate treatment was introduced, in 1873, by Dreisch (see 11), who suggested an after treatment of the soaked seed by immersion for five minutes in milk of lime. What reason prompted such a proposal is not given, but it had been the old practice, according to Tull, to sift quicklime over the heap of " brined " seed. The object here was evidently

to hasten the drying of the seed, though Tull stated that the quick-lime confined the brine to the surface of the grains and " suffers none of it to be exhaled by the air." In this fashion were the basic copper seed disinfectants introduced, materials which survive to-day in the copper carbonate dusts.

From 1860 to 1895, the search for a suitable substitute for copper sulphate, which was found to have an objectionable action upon the seed, continued. Hollrung (11) has given the history of this period in much detail. The most promising of the materials tried appears to have been salicylic acid, suggested by Schröder in 1892, which however suffers from the disadvantage of expense. Keller-man and Swingle, in 1891, found in liver of sulphur (potassium polysulphide) a satisfactory disinfectant. This material is of interest, too, in that it formed the active agent of " Ceres " powder, a seed fungicide placed on the market by Jensen, the originator of the hot-water treatment (see p. 274). Sulphur has latterly been found of great value as a seed dressing for recommendation where a cheap, simple and foolproof method is essential.

About 1890, a new field was opened by Bolley (12) who, for the control of potato skin diseases, immersed the " seed " in mercuric chloride. At the beginning of the century, Hiltner employed this compound for the control of cereal diseases. From his success and from experience with salicylic acid may be traced the development of the organo-mercury seed disinfectants.

In 1895, the then new disinfectant, formaldehyde, was intro-duced for the treatment of cereals. For some time, formaldehyde proved one of the most popular of the seed disinfectants until the development of the copper carbonate and the organo-mercury dusts.

From this brief historical survey it will be seen that the materials available for seed treatment purposes fall into the copper, sulphur and mercury groups and formaldehyde.

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The Copper Group.

The older treatment with copper sulphate solutions necessitated a complete submersion of the seed. Such a procedure, especially when it entailed after-treatment with milk of lime, was too cumbersome for the average farmer. It required special vats and apparatus for hoisting the sacks of grain. The grain itself took up large amounts of water and therefore took a long time to re-dry. Under such circumstances the possibility of after-infection of the grain was enhanced. It is perhaps here that, with the copper sulphate treatment, the after-treatment with lime water would be of value, for insoluble copper compounds are formed which continue to protect the grain.

To ease the labour involved in the immersion method, the " heap " method was introduced in which the heap of grain was sprinkled with a solution of 1 to 10 per cent. bluestone at the rate of one gallon per sack of wheat. The heap was then shovelled until all the grain was wetted, afterwards being spread out to dry. The method has the advantages of simplicity, that no special apparatus (apart from a suitable floor protected from re-infection) is required and that, as less water is taken up by the grain, less time is taken for it to dry.

The heap method was, until the introduction of formaldehyde, widely used in this country (13) for the control of Bunt of Wheat (*Tilletia caries* and *T. fœtens*). It ultimately proved unsatisfactory mainly because of seed injury. That the extent of seed injury was correlated with the extent of seed damage during threshing was established by Nobbe (14). This relationship was explained by the work of Brown (15), who showed that the uninjured seed coat, though permitting water to pass into the seed, excluded salts such as copper sulphate. If, then, the seed coat be whole, copper cannot penetrate to and injure the embryo.

Dry treatment with copper fungicides was not generally adopted until after 1917, when Darnell Smith (16), in Australia recommended basic copper carbonates for the control of Bunt. It was estimated that, in 1925, one-tenth of the total wheat acreage of the United States was sown with seed treated with copper carbonate, with a net gain of at least five million bushels (17).

The basic copper carbonates of commerce are generally assumed to approximate in composition to malachite, $Cu(OH)_2CuCO_3$, and, allowing for impurity, such a compound would correspond to the standard proposed by Mackie and Briggs (18). Leukel (19) stated

that the better grade of copper carbonate marketed in the U.S.A. was of this formula but that cheaper grades, usually sold under trade-names, contained but 18–25 per cent. metallic copper with sulphate or other ingredients. Southern (20) also found that the products used in Australia included basic sulphates and basic chlorides. He was unable to find a better test than copper, content to distinguish the inferior products though, on the whole, the basic sulphates and mixtures of basic sulphates and carbonates proved better than the basic carbonates and basic chlorides tested.

The action of copper salts upon the bunt spore is generally held to be associated with an adsorption of cupric ions on the spore membrane. Bodnár and Terényi (21), in addition to showing that the amounts of copper taken up by bunt spores accorded with the adsorption equation, confirmed earlier reports that leaching of the treated spores with hydrochloric acid restored their ability to germinate. Terényi (22) confirmed these results with *Ustilago avenœ* but found that, after prolonged steepage, ability to germinate was no longer restored by acid treatment, indicative of a penetration of copper into the spore.

The mode of formation of cupric ions from the basic " carbonates " was investigated by Southern who, although obtaining suggestive results, was unable to confirm Pickering's hypothesis that carbon dioxide is the primary agent causing the solution of copper. It is evident, from his figures, that the fungicidal efficiency of any single chemical factor is affected by circumstances such as degree of fineness and soil conditions.

The dry copper carbonate treatment was found, by Dillon Weston (23), to be effective in controlling bunt on slightly contaminated seed and, following a comprehensive test against the older " pickling " or heap methods, Pethybridge and Moore (24) reported that the dry method was worth comparison by growers with the older methods. Against other cereal diseases, Tisdale, Taylor, Leukel and Griffiths (25) found copper carbonate less effective against Covered Smut of Barley, *U. hordei* (Pers.) Lagerh., and Loose Smut of Oats (*U. avenœ*). Heald, Zundel and Boyle (26) reported that copper carbonate was effective both for Bunt of Wheat and Smut of Oats (*U. kolleri* Wille), being more effective on the hull-less varieties of oats than on the commoner varieties.

The use of copper derivatives as seed protectants against *Pythium ultimum* Trow and other soil fungi, was developed mainly by Horsfall (27) who first experimented with mono-hydrated copper

sulphate (28). Later (29) he selected cuprous oxide which, because of its better adherence and high copper content, enabled the seed to retain a greater amount of fungicide. Horsfall, Newhall and Guterman (30) enumerated many varieties of plant which benefited by the treatment, but recorded damage to the cabbage family, for which zinc oxide treatment was recommended (31). Frictional difficulties met in drilling treated seed were overcome by the addition of powdered graphite as a lubricant (32).

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Formaldehyde.

Formaldehyde, discovered by Hofmann in 1867 and first employed as a disinfectant by Loew in 1888, was introduced as a seed disinfectant by Geuther (33) in 1895. Its use for the purposes of seed treatment did not apparently become widely spread until it was employed in Germany, owing to the shortage of copper in 1914–18, as a substitute for copper sulphate. In England, its use followed mainly, despite the earlier recommendation of Johnson (34), from the work of Salmon and Wormald (35). These workers found that the germination injury caused by formaldehyde is less serious than that caused by the copper sulphate treatment.

As to the action of formaldehyde upon the fungus spore, little is known. Hailer (36) showed that the inhibition of the germination could be prevented by the timely addition of sulphite (the condensation with a sulphite is a characteristic reaction of formaldehyde). With a prolonged action, however, Hailer concluded that an irreversible complex of formaldehyde and the amino groups of the spore protoplasm is formed.

Further, it was found that unless the grain was sown immediately after treatment, germination injury became severe. McAlpine (37) noted that storage after treatment and prior to sowing, resulted in a serious decrease in the percentage of germination, a fact he attributed to the hardening of the seed coat by the action of the formaldehyde. This pronounced injury due to delay in sowing after treatment has been confirmed by later workers (38), and has been also attributed to a formation of paraformaldehyde, a polymer of formaldehyde. If the grain be dried rapidly after formaldehyde treatment, injury is less severe. In the heap method it is therefore necessary to spread out the grain after treatment, in order to secure the maximum aeration and so facilitate the evaporation of the paraformaldehyde.

As to the nature of the injurious effect observed, Atwood (39) has shown the slow penetration of formaldehyde through the seed coat with the result that diastatic activity is retarded and the respiration of the seed is weakened. Mackie and Briggs (40) stated that, whereas copper sulphate appears to repress the root growth of the seedling, formaldehyde interferes with the development of the plumule.

Formaldehyde appears to be useless as a seed protectant, indeed Machacek and Greaney (41) found that it increased attack of cereals by " Foot-rot " (due to soil fungi such as *Fusarium culmorum* (W. G. Sm.) Sacc. and *Helminthosporium sativum* Pamm., King & Bakke) probably by retarding the growth of the seedlings.

The treatment of seed potatoes for two hours in a 1 : 240 dilution of 40 per cent. formalin was suggested by Arthur (42) for the control of Scab, *Actinomyces scabies*. To avoid the lengthy immersion, Melhus, Gilman and Kendrick (43) tried the effect of increasing temperature and found that a five-minute immersion at 48–50° C. was as effective as the cold treatment against both Scab and the Rhizoctonia disease (*Corticium solani* Bourd. & Gaez).

Injury to the sprouting of the seed tubers resulted only if the temperature was raised above 55° C.

It must be remembered, however, that these potato diseases can

also be soil-borne. The tuber treatment is therefore of secondary importance until it be established that there is no danger of soil infection.

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The Sulphur Group.

Apart from the polysulphides, recommended by Kellerman and Swingle (44) and the " Ceres " powder of Jensen, little use has been made of sulphur and its compounds as fungicides for seed treatment. Mackie and Briggs (45) found dry treatment with flowers of sulphur effective for the control of Bunt and, in 1923, Uppal and Malelu (46) successfully used sulphur for the control of Grain Smut of Millet, *Sphacelotheca sorghi* (Lk.) Clinton, a success which led Howard Jones (47) to include sulphur in his trials upon the control of Covered Smut of Barley (*U. hordei*). The simpleness and foolproof character of the process rendered it suitable for recommendation to native Egyptian farmers following but primitive agricultural methods. Howard Jones recommended sulphur treatment of the grain as soon as possible after harvest, for the sulphur afforded a useful measure of protection against insect pests during storage.

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The Mercury Group.

The powerful bactericidal action of mercuric chloride (Corrosive Sublimate, $HgCl_2$) naturally led to its trial as a seed disinfectant.

For the treatment of cereal grain it was tested by Kellerman and Swingle (48), but without great success. Hiltner (49) later found it valuable for the control of Fusarium Disease of Rye (*Calonectria graminicola* (Berk. and Br.) Wr., and a number of preparations (e.g. Fusariol, Fusafine) incorporating mercuric chloride, were placed on the market. The significance of Hiltner's discovery is that the Fusarium Disease is not carried over by spores on the exterior of the grain but by a dormant mycelium within the seed. The fungicide must remain on the seed to prevent infection of the coleoptile. Hiltner's observation thus indicated the possibility of utilizing a protective fungicide for the control of diseases carried over within the seed, of which examples are the Helminthosporia and the Loose Smut of Wheat, *Ustilago tritici* (Pers.) Rost. and of Barley, *U. nuda*.

For pharmaceutical purposes, mercuric chloride was, on account of its intense poisonous properties, replaced by organo-mercury derivatives. According to Bonrath (50), G. Wesenberg, of the I.G. Farbenindustrie A.-G., first suggested the use of such materials as seed disinfectants. The first record of their use is by Riehm (51), who, in 1914, reported " Chlorphenol-mercury " successful for the control of Bunt. The development of the organo-mercury seed disinfectants has been due entirely to the activities of interested commercial firms and, as little of this work has been published, this development can be traced only by a review of the materials which have been placed on the market and which may be presumed to mark definite advances in the investigations of the manufacturers.

The true organo-mercury derivatives are those in which the mercury atom is attached direct, by one or both valency bonds, to carbon atoms. The general structure of those derivatives found as the active constituents of seed disinfectants is R.Hg.X, where R represents a hydrocarbon with or without substituent groups, and X represents an acidic radical.

Reviewing the more important of the proprietary seed disinfectants, the first was Uspulun, placed on the market in 1915 by Fr. Bayer in Germany, following successful trials by Riehm and others. The active constituent of this product was described as " chlorphenol-mercury " probably of the structure Cl(OH)C$_6$H$_3$.Hg.OSO$_3$Na, though it is not clear from the manufacturer's statement whether the salt-forming group was hydroxyl or sulphate. The product, which contained 18·8 per cent. metallic mercury, was intended for the steeping or pickling method and,

as relatively large amounts of alkali were required for its solution, Uspulun contained sodium hydroxide and a colouring matter added to conform to poisoning regulations. The success of Uspulun led to the introduction of a number of similar products, in particular, Semesan of Du Pont de Nemours in the United States brought out in 1924. Germisan, introduced about 1920 by the Saccharin Fabrik A.-G., contained 16·1 per cent. metallic mercury in the form of cresyl mercuric cyanide, $(HO)(CH_3)C_6H_3.Hg.CN$. Bonrath (50) stated that the employment of cyanide, iodide or complex cyanides to satisfy the second mercury valency added to the efficiency of the mercurated cresols.

The adoption of the dry treatment with basic copper carbonate resulted in the introduction, by Fr. Bayer in 1924, of organo-mercury dusts, of which the first was Uspulun " Trockenbeize," later called Tillantin-R in Europe and Bayer Dust in the United States. The active constituent of this product was stated to be an *ortho*-nitro phenol mercury derivative, probably represented by $(HO)(NO_2)C_6H_3.Hg.OH$, the dust containing 3·4 per cent. metallic mercury.

Following the amalgamation of the commercial interests, the next important group of products are noteworthy in that their organic radicals, instead of being phenolic, were hydrocarbon groups with no substituent groupings. Ceresan, introduced by the I.G. Farben-industrie A.-G. for the European market, was reported to have as the active ingredient phenyl mercuric acetate, $C_6H_5.Hg.O.CO.CH_3$, and to contain 1·5 per cent. metallic mercury. Agrosan G., introduced by I.C.I. Ltd., contained a like amount of mercury in the form of tolyl mercuric acetate, $CH_3.C_6H_4.Hg.O.CO.CH_3$. Ceresan, introduced by Bayer-Semesan Co. Inc., for the American market, and a similar product Granosan in this country (52), are said to contain 2·0 per cent. ethyl mercuric chloride $C_2H_5.Hg.Cl$, though the figure 2·0 may refer to the content of metallic mercury. This product was later replaced, in America, by New Improved Ceresan, containing 1·3 per cent. mercury in the form of ethyl mercuric phosphate, $C_2H_5.Hg.H_2PO_4$.* Recently, the composition of European Ceresan has been altered, the new derivative used being described by Bonrath as " an ether of a mercurated alcohol." An interesting point is that this expression would infer that the use of substituent groupings of the hydrocarbon R has again

* It is not apparent, from the maker's description, whether the compound is a normal or acid phosphate.

appeared, perhaps in the form R'.O.R''.Hg.X, in which R' and R'' represent hydrocarbons. Bonrath stated that the corresponding esters, which would then be represented by R'.CO.OR''.Hg.X, have markedly lower fungicidal properties. The practical value of the ether type of organo-mercury derivative rests in its suitability not only for dusts but for the new short steepage process now being employed in Germany (53). The product for dry treatment, Ceresan UT1875a, contains 1·5 per cent., that for wet treatment, Ceresan U564, 2·5 per cent. metallic mercury.

The correlation of molecular structure and fungicidal efficiency of the organo-mercury compounds has formed the subject of but three communications. The first, by Riehm (54), concerned the application of Ehrlich's chemotherapeutic technique to seed disinfectants. Riehm determined the *dosis curativa* by which Ehrlich referred to the minimum concentration of the therapeutic product which will effect a cure, as the minimum concentration necessary to inhibit the germination, under standard conditions, of bunt spores. The maximum concentration without deleterious effect upon germination, Riehm termed the *dosis tolerata*, a term by which Ehrlich described the maximum dose which the patient can tolerate. Gassner and Esdorn (55) applied Riehm's methods to organo-mercury derivatives and, amongst other points of interest, showed the profound influence of structure upon the fungicidal properties of these compounds. Thus, the *dosis curativa* of mercuric chloride was found to be 0·025, that of mercuric cyanide was greater than 10 ; that of compounds similar to those present in Uspulun, Germisan and Tillantin-R was between 0·07 and 0·12, whereas that of methyl mercuric iodide was as low as 0·001. The last-named compound, although by far the most active of the compounds tested, was discarded by Gassner and Esdorn on the score of its highly poisonous character. It will be noted, however, that in this compound, R is a hydrocarbon without substituent groupings. To this observation and to the work of Klages (see 50), the introduction of the mercurated hydrocarbons as seed disinfectants is due.

The third communication, that of Dillon Weston and Booer (56), was concerned with an examination of the properties of inorganic mercury compounds and of organo-mercury compounds in which R is a hydrocarbon. The majority of the inorganic compounds were found to be of little value as seed fungicides. The series of organo-derivatives in which R was limited to the tolyl, C_7H_7—, phenyl, C_6H_5—, ethyl, C_2H_5—and methyl, CH_3—groups, were

employed against *Helminthosporium avenœ* (Bri. and Cav.) Eid., *H. gramineum, U. avenœ* and *T. caries,* and the results indicated that fungicidal properties decreased with increase of molecular weight of the hydrocarbon group. As factors other than actual toxicity are involved in the determination of practical value, this conclusion was not accepted as meaning that dusts containing phenyl (or tolyl) compounds are necessarily less effective in disease control than those containing ethyl or methyl compounds. Dillon Weston and Booer also examined the influence of the acidic group X upon the fungicidal efficiency of the methyl compounds and, although their results would suggest that the iodide, which Gassner and Esdorn found the most effective of the compounds they tested, was relatively inferior to the chloride or phosphate, Dillon Weston and Booer derived no conclusions upon the point in the preliminary outline of their work.

From the investigations of Gassner and Esdorn and of Dillon Weston and Booer, it is evident that the fungicidal efficiency of organo-mercury compounds is determined by factors in addition to content of metallic mercury. In this connection, it may be noted that the compounds employed in the proprietary products show an increase in potency. Whereas the first steepage material, Uspulun, contained 16·8 per cent., the latest form of Ceresan for steepage treatment contains 2·5 per cent. metallic mercury. The first dust, Tillantin-R, contained 3·4 per cent., but Ceresan UT1875a contains but 1·5 per cent. metallic mercury.

The progress made in the development of the organo-mercury seed disinfectants is also reflected in the range of diseases effectively controlled by these products. Uspulun, Germisan and the similar products were primarily protectant in action and found their greatest use against the Helminthosporia. Thus, Tisdale (57), summarizing general experience up to 1926, reported that all were excellent for the steepage treatment of barley. For oats, he considered it doubtful whether they were more effective than formaldehyde ; for wheat, he considered them less effective than basic copper carbonate. In 1929, Tisdale and Cannon (58) reported that ethyl mercuric chloride was effective for the control of Bunt, of Covered Smut and Stripe of Barley and of Smut of Oats. The transition from products of specific fungicidal properties to products of general fungicidal properties is of fundamental importance in the history of synthetic fungicides.

Against diseases other than the seed-borne cereal diseases,

mercuric chloride has been mainly used for the treatment of " seed " potatoes. Bolley (59) found it a most promising agent against Potato Scab and it has since been used in the United States for the control of Scab, Rhizoctonia disease and Powdery Scab (*Spongospora subterranea*). For these purposes it has been found, on the whole, to be more effective than formaldehyde. Leach, Johnson and Parson (60) recommended an acid-mercuric chloride treatment, the tubers being immersed for five minutes in a solution of 1 in 500 mercuric chloride containing 1 per cent. commercial hydrochloric acid. They pointed out that this treatment will not always give perfect control as the diseases are not exclusively seed-borne. The extension to organo-mercury disinfectants followed and a short immersion (" instant dip ") with suspensions or solutions of these compounds was found by Clayton (61) more satisfactory than mercuric chloride treatment. The greater convenience of the instant dip method led to its recommendation by Cairns, Greeves and Muskett (62) for the control of *Actinomyces scabies* and by Greeves and Muskett (63) against Skin Spot, *Oospora pustulans* Owen and Wakef.

The use of organo-mercury compounds for seed protection was examined by Brett, Dillon Weston and Booer (64) and recommended for early-sown peas. As the success of seed protection is determined also by the rapidity of emergence and establishment of the seedling, the possible use of substances promoting root-formation and growth (phytohormones) in combination with seed protectants was obvious. Grace (65) used phytohormones to overcome the injurious effects of formaldehyde treatment on germination, but their use with cuprous oxide and with organo-mercury compounds was investigated by Croxall and Ogilvie (66).

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Action on the Fungus Spore. As with other heavy metals, the toxic action of mercury is generally ascribed to an adsorption of mercuric ions which, in the case of spores of *T. caries*, was shown by Bodnár and Terényi (67) to conform to the general adsorption equation. Upon this hypothesis, the non-ionized mercuric compounds, such as mercuric cyanide, should be deficient in fungicidal properties, a conclusion confirmed by Gassner and Esdorn (see p. 269) and by Bodnár and Terényi. The latter workers showed, however, that spores treated with mercuric chloride or bromide did not germinate when sown upon calcium nitrate media or upon moist soil, under which conditions those treated with mercuric acetate germinated. As the amount of adsorbed mercury on the latter spores was greater, the quantity of adsorbed mercury is not the sole criterion of fungicidal efficiency. Bodnár and Terényi suggested that the difference is associated with the adsorption, not of mercuric ions, but of mercuric chloride or bromide molecules which, by virtue of their lipoid solubility, can penetrate within the spore membrane. A similar explanation was put forward by Walker (68), who showed that phenyl mercuric chloride and allyl mercuric chloride, were more toxic than mercuric chloride to the protozoon *Colpidium colpoda*. He associated this greater toxicity to the greater lipoid solubility of the organo-mercury compounds. That lipoid solubility is a factor determining toxicity is the basis of the Overton-Meyer theory (see p. 305). An alternative hypothesis, that metallic mercury, formed from mercury compounds by reduction in the soil, is the active fungicide, was tested by Daines (69).

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Action on the Seed. Apart from one effect, the organo-mercury disinfectants appear to be harmless to the seed. The exception is a characteristic hypertrophy of cereal seedlings induced by disinfectants containing compounds of the R.Hg.X type (56, 70) when these are overdosed or the treated seeds incorrectly stored. The plumule and radicle of the injured seed fail to elongate but remain swollen, a malformation attributed by Sass (71) to incomplete mitosis.

It has frequently been claimed, as with the basic copper carbonates, that the treatment has a favourable influence. Stützer (72), for instance, found that Uspulun had a stimulating effect not only upon germination but upon the whole development of the plant. Confirmatory reports from Germany are numerous, whilst in the United States, Tisdale, Taylor and Griffiths (73) secured a similar result with a related product " Chlorophol."

The establishment of the existence of this stimulation is a matter of extreme difficulty, for it must be shown that the improved growth is not due to the destruction of soil fungi and bacteria which are normally present in the control. Such fungi and bacteria might of course cause direct injury to the germinating seed of the control plot or their effect might be more indirectly detrimental in that they utilize oxygen needed by the germinating seed. Sampson and Davies (74), by trials with bunt-free seed treated with either Uspulun, Tillantin or basic copper carbonate, concluded that stimulation was attributable solely to the fungicidal properties of the disinfectant which inhibited the growth of organisms present in the soil or on the seed.

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Fillers for Mercury Dusts. For the dilution of organo-mercury compounds when to be used as dusts, various finely-divided inert mineral carriers or fillers are used, but references to the effect of type of filler upon fungicidal efficiency are few. It would appear that the filler should be sufficiently adherent to the seed, yet should not interfere with drilling operations. Dillon Weston and Booer (56) obtained an indication that fillers of a highly adsorptive char-

acter may adversely affect disease control, whilst Stirrup (75) recorded that, for use upon sugar-beet seed, results have shown that the filler should preferably be of an alkaline nature.

To reduce dustiness, in view of the noxious character of the organo-mercury compounds, the majority of the proprietary seed disinfectants contain an anti-dust, usually of an oily character (e.g. B.P. 241568). Dillon Weston and Booer found that the addition of oil had no deleterious action in the case of the compound and dust they tested.

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PHYSICAL METHODS

The development of the use of heat as a seed disinfectant was due to Jensen (76). In 1882, he demonstrated that the hyphæ and spores of *Phytophthora infestans*, which grew in or on diseased potato tubers could be killed by a four-hour treatment in a current of hot air at 40° C. His method was used against Potato Blight until 1886, the date of the introduction of Bordeaux mixture.

In 1887, for the prevention of Smut in oats and barley, Jensen (77) found that the various chemical steeps then known were ineffective, but that treatment with hot water gave, at least with oats, a satisfactory measure of control. Prior to this, Sinclair (78) had suggested treatment with hot air from an oven, a process which Jensen found ineffective even after an exposure for seven hours at $51\frac{1}{2}$–54° C. Jensen, noting that the control of the Loose Smut of Barley was not so complete as that secured by his method with oats and that hot-air treatment was ineffective, concluded that moisture plays some rôle other than that of mere heat transfer. He considered that the Smut " germ " when moistened was more vulnerable and so proposed his " modified hot-water treatment " in which the seed is immersed in cold water before treatment with hot water. This pre-treatment was placed on a scientific basis by Appel and Riehm (79), who showed that, by a four-hour treatment in water at 20–30° C., the dormant mycelium develops activity and is more easily killed by a short exposure at 50–52° C.

The modified hot-water treatment is, despite its cumbersomeness, still used to-day against the Loose Smut of Wheat, *U. tritici*, and

of Barley, *U. nuda*, in both of which the fungus is carried over as a dormant mycelium within the seed.

Hot-water treatment has also been found effective for the control of certain nematodes. Ramsbotton (80) extending the earlier work of Fryer (81) showed that the immersion of narcissus bulbs for one hour in water at 110° F. reduced the attack by *Anguillulina dipsaci* (Kühn) Gerv. and v. Ben. In its present form (82), the standard treatment is for three hours at 110° F., under which conditions the eelworms within the bulbs are killed whilst the bulbs survive. Similarly, for the control of eelworm disease of chrysanthemum, due to *Aphelenchoides ritzemabosi* Schwartz, the infested stocks are immersed in water maintained at 110° F. for twenty minutes (83, 84, 85). A recent application of the method (86) is for the control of Tarsonemid Mite of Strawberry (*Tarsonemus pallidus* Banks). A clean stock is obtained by the immersion of the runners in water held at 110° F. for twenty minutes (87). In view of the high phytocidal properties of temperatures above 110° F., Massee preferred to call the method a warm-water treatment.

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SOIL TREATMENT

Under " Soil Treatment " are classed those methods of pest control which aim at the destruction of the pest in the soil itself. Certain types of pest in the soil, such as the wireworms (the larvæ of Click-beetles, Elateridæ) and the parasitic eelworms (Nematodes), destroy the root tissues ; others gain entry to the plant via the roots, for example, certain fungi and other " biological factors," to which are attributed cases of soil sickness. The methods of control fall under two heads—firstly, the treatment of the soil by physical and chemical means whereby the injurious organisms are killed directly. To this category would also belong the less drastic cultural modification of the soil to render it unsuitable for the noxious organism, a treatment already mentioned on page 40. As the destruction of all soil organisms would be harmful to subsequent plant growth, the aim is to secure a partial sterilization of the soil to the benefit of the plant. Secondly come the mechanical methods of which the most important is " Crop Rotation " which, by withholding the host plant, aims at the starvation of the harmful organism.

PARTIAL STERILIZATION

Partial Sterilization has assumed great importance, especially to the horticulturist, from the fact that it results not only in the destruction of harmful organisms but also in a great increase in the fertility of the treated soil. Indeed in certain cases, partial steriliz-ation of the soil has now become, as a result of this increase of yield, not so much a measure of pest control but a cultural operation profitable because of its relationship to the nutrient supply. It would be impossible to enter at all fully into the work which has so far been carried out upon this " manurial " aspect of Partial Sterilization.

*" Soil Sickness " is a popular term applied to the condition of a

soil which, although showing no lack of nutrient material, fails to yield a satisfactory crop. It generally appears in soils which under an intensive system of cultivation have grown one crop continually, conditions which would encourage the growth of the disease organisms and pests of that crop. This condition may be due, in part, to the deterioration of the physical properties of the soil by heavy dressings of artificial manures and watering and may then be alleviated by the incorporation of straw in the soil by the method described by Bewley (1). In other cases, soil sickness has been traced to a superabundance in the soil of definite organisms, for example, Root Knot due to the eelworm *Heterodera marioni*, Flax Sickness due to the fungus *Fusarium lini*, Clover Sickness, one type of which is due to the eelworm *Anguillulina dipsaci* and another type to the fungus *Sclerotinia trifoliorum* Erikss. Moreover, if the theory that soil sickness results from the presence of biological " limiting factors " such as protozoa or organisms detrimental to the beneficial soil bacteria be accepted, Partial Sterilization still remains a true method of pest control.

The first observations of the increase of yield following partial sterilization were made independently by Girard (2) and by Oberlin (3) in 1894. These workers had employed carbon disulphide as their sterilizing agent. Similar results were found after the application of other volatile antiseptics, and in 1907, Darbishire and Russell (4) showed that partial sterilization by heat produced a like result.

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Heat.

It has been suggested that the old practice of exposure of the soil to the heat of the sun, still carried out in India, has as its basis, partial sterilization. Prescott (5) suggested that the " sheraqi " fallow, a feature of Egyptian cultivation during which the soil is left fallow at the hot period, may secure a partial sterilization of the soil. Drying out of the soil may bring about similar results and Lebediantzeff (6) showed that the fertility of the Russian soils with which he worked was increased by air-drying.

Practical difficulties render the partial sterilization of large areas

of soil by heat impossible. Fortunately those areas which show the greatest need for treatment are sufficiently small for the purpose. It is mainly in glasshouses, seed and frame beds, especially where the same crop is grown continually, that the climatic and nutritive conditions are so favourable for the rapid multiplication of soil pests and fungi. It is therefore just these soils which show the greatest need for partial sterilization.

To secure the beneficial effects of partial sterilization the soil should be maintained at a temperature of 97° C. (207° F.) for one hour. Various methods are now available for the economical heating of the soil to the required temperature (7). For the small grower the baking of small quantities of soil in a suitable oven is satisfactory, provided that a careful control of temperature is possible. It is of course necessary to guard the soil from re-infection after treatment. The labour of moving the soil is saved by the use of steam as the heat-carrying agent. The general procedure of such methods is to conduct steam, at high or low pressure, into the soil until the temperature required is reached and maintained. In the United States, the " inverted steam pan " method, introduced in 1909 by Gilbert, is a popular method of soil treatment by heat (8). Electrical methods of partial sterilization or pasteurization of batches of soil are now being examined (9).

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Chemical Methods.

Theoretically the application of a toxic chemical to the soil should be a far simpler matter than its application to foliage. It is possible to apply the material when the soil is fallow and provided that it disappears by volatilization or by decomposition before planting there should be no damage to the plant. But trouble is encountered, firstly, because for the economical treatment of large areas of soil it is essential that the chemical should be cheap. Secondly, there are difficulties in securing the penetration of the toxic agent which must reach to the greatest depth occupied by the organisms against which it is to act. For this purpose it is preferable that the substance should be either a gas or a liquid or,

if a solid, should be either volatile or capable of solution or emulsi-
fication in water.

In the treatment of soil sickness it is usual to describe the chemical
employed as an " antiseptic," whereas if volatile and against a
definite pest, the name " soil fumigant " is more frequent.

The requirements of such antiseptics and soil fumigants may then
be summarized briefly thus : (i) cheapness ; (ii) good penetration
into the soil ; (iii) non-injuriousness to the plant either direct or
through a deleterious action upon the physical properties of the
soil.

Dealing then with those chemicals which have found practical
use for partial soil sterilization, in its broadest sense, one of the
most interesting historically is :

Carbon Disulphide. This substance was originally employed
in 1872 by the French chemist Thénard, against the dreaded Phyl-
loxera of the vine (*Phylloxera vastatrix*). His method was to
inject the required amount of carbon disulphide into the soil at
distances around the infected vine. The treatment was so highly
successful that by 1887 over 66,000 ha. of land were so treated in
France alone (10).

Carbon disulphide has the advantages of cheapness, volatility
and good insecticidal properties. It was, at one time, thought
that the density of its vapour would permit it to sink into the
soil but Higgins and Pollard (11) concluded that the movement
of the vapour was largely a simple diffusion process obtaining no
evidence of marked gravitational flow. The diffusion was also
studied by O'Kane (12) and by Fleming (13), the general conclusion
being that carbon disulphide is rapidly lost by evaporation espe-
cially from the surface layer, a loss not adequately prevented by
covering the surface with sacking. Further it was found that,
though penetration is good in sandy or humus soils of not too
great a moisture content, it was inefficient in moist, or heavy clay
soils. Fleming deduced the interesting point that part of the
original carbon disulphide is taken up by the soil and that by a
second treatment, the persistence of the vapour in the soil is greatly
enhanced.

To overcome the objection of rapid loss of the carbon disulphide
by evaporation, a number of compounded products have been put
on the market, notably on the Continent. " Sulphoergethan," a
preparation of carbon disulphide and tetrachlorethane in the form
of a cake which when buried in the soil slowly evolves carbon

disulphide was found unsatisfactory by Börner and Thiem (14). The latter workers also found that a trade preparation of carbon disulphide and nitro-benzene under the name " Horlin " was no more efficient than carbon disulphide alone.

To overcome the objection of the fire hazard of carbon disulphide, which adds greatly to the transit costs of this material, Truffaut (15) proposed the employment of an emulsion of carbon disulphide. Leach, Fleming and Johnson (16) have recommended the use of an emulsion of carbon disulphide and wormseed oil for the control of the soil stages of the Japanese beetle.

An interesting modification of the carbon disulphide treatment was suggested in 1874 by Dumas (17), who proposed the use of potassium sulphocarbonate (thiocarbonate), K_2CS_3. This material was placed on the market, in France, in the form of a dark red solution containing 18–20 per cent. potash. As it is soluble in water, penetration into the soil is good provided that the soil be sufficiently watered. Under the action of carbon dioxide, the compound decomposes with the evolution of carbon disulphide. The material is therefore slower in action than carbon disulphide but is more persistent. Its efficiency as an insecticide has been well established but, despite a plea by Molinas (18) for its continued use, its employment has not spread beyond the vine-growing centres of France. Possibly the cost of the treatment is prohibitive although its manurial value due to the potash present is high. Indeed as the effects of any form of partial sterilization of the soil on the succeeding crop are similar to those of a nitrogenous manuring, the need for potash becomes greater in order to secure the best use of this result and to maintain the nutrient balance requisite for the health of the plant (see p. 38).

<div align="center">REFERENCES</div>

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Coal-tar Antiseptics. The commercial coal-tar antiseptics, in

use as disinfectants, suggested themselves as suitable products for partial sterilization of soil. Hiltner (19) had proposed the employment of carbolineums (see p. 203) as cheaper than carbon disulphide and as being not only effective in raising the fertility of the soil but efficacious against soil pests and weed seeds. Molz (20) reported favourably on the carbolineums, especially those prepared from the lighter tar distillates, as soil insecticides against nematodes. An objection to their use, pointed out by Nostitz (21), was that the carbolineums, though efficient soil antiseptics, harmed subsequent plant growth unless applied some five months before sowing.

Russell (22) and his colleagues found a cheap and effective antiseptic in cresylic acid (liquid carbolic acid, pale straw coloured, 97–99 per cent. purity), a product of the crude tar acids consisting mainly of phenol and the three isomeric cresols. These compounds are decomposed with sufficient rapidity in the soil to ensure no harmful effect on subsequent crops. The diluted cresylic acid is either " watered " on to the soil or is mixed with dry soil containing gypsum and then dug in. Of the constituents of cresylic acid, phenol and o-cresol appear to have about the same toxic value (23) whilst the m- and p- cresols do not appear to be quite so effective (24).

A systematic examination was carried out at Rothamsted of the pure aromatic derivatives which are derived from the tar oils. The requirements of a soil insecticide are toxicity towards soil pests coupled with a relative instability to give products harmless to subsequent plant growth. It was found that the introduction of chlorine into the aromatic compound led to an increased toxicity. Dichlorcresylic acid, for example, was more effective than cresylic acid. Extending this work, Matthews (23) found that the chlorine group by itself or with a nitro-group, or two chlorine groups and one nitro-group produced great stability. On the other hand, one or two nitro-groups or two nitro-groups and one chlorine group gave an unstable product. Thus, chlordinitrobenzene was superior in toxicity towards eel-worm, fungi and protozoa to nitrodichlorbenzene and further was more easily and rapidly decomposed in the soil. According to Russell (25), however, this decomposition is not sufficiently rapid to prevent the injurious action of chlornitrobenzene upon plants.

*Para*dichlorbenzene has been successfully used as a soil fumigant in America. This material appears to have been first used by Blakeslee (26) for the control of the Peach-tree Borer *Sannonoidea*

exitiosa Say. The more usual soil fumigants were unreliable against this pest under field conditions but this compound while sufficiently volatile to prove toxic to the larvæ, did not injure those trees over six years of age. According to Essig (27), the best results are secured at soil temperatures of 75–83° F., and it is possible that in regions where such soil temperatures are usual, the material may prove a valuable insecticide against other pests. *Para*dichlorbenzene appears on the market, in the United States, under the name of P.D.B., or Paracide.

The increased activity due to the introduction of chlorine into the molecule is again well shown in the case of the chlorethylenes. Schwaebel (28) showed that, whereas an increase in yield follows treatment of the soil with both dichlorethylene, CHCl:CHCl, and trichlorethylene CHCl:CCl$_2$, tetrachlorethylene CCl$_2$:CCl$_2$ is so toxic that it brings about a reduction of fertility. The association of chlorine and a nitro-group in chlorpicrin (trichlornitromethane, CCl$_3$.NO$_2$) gives a highly efficient soil fumigant, but the material is too inconvenient to handle and is too dangerous for ordinary use (29).

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Formaldehyde. Formaldehyde was apparently first recommended for soil treatment by Gifford (30), who found it more effective, for his particular purpose, than steam. It was further recommended by Russell and Petherbridge (31) as the most effective antiseptic that they had, at the time, tried. It is volatile and has the advantage of being soluble in water, appearing on the market in aqueous solution under the name Formalin. The solution should contain not less than 36 and not more than 40 per cent. weight in volume of formaldehyde and may contain up to 14 per cent. methyl alcohol to delay polymerization to paraformaldehyde.

A special advantage of formaldehyde was revealed by Hunt,

O'Donnell and Marshall (32), who showed that its penetration is apparently equal to that of the water carrying it in solution. This result would indicate that, with formaldehyde, there is no adsorption of the toxic material by the soil, the cause of the poor penetration of most of the antiseptics employed for soil treatment.

The disadvantages of formaldehyde, of which usually 2–3 quarts of a 0·5 per cent. solution are added per square foot of soil, are the general objection that the soil takes too long to re-dry ; that the fumes of formaldehyde may cause a retardation or reduction of germination ; but more important that formaldehyde, although an efficient soil fungicide, has but slight insecticidal properties.

<div align="center">REFERENCES</div>

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Miscellaneous Partial Sterilizing Agents. Apart from fungicides added to the soil against specific soil-borne diseases, the search for a suitable soil antiseptic has so far failed. The most promising used to date appears to be :

Calcium Sulphide. Russell and Petherbridge (33) used this compound in the form of gas lime. In the older methods for the purification of coal gas, lime was employed to remove the sulphur compounds. The spent material, " Blue Billy," so obtained, contained a large proportion of calcium sulphide and, in some cases, calcium thiocarbonate formed from carbon disulphide present in the impure coal gas. This material Russell and Petherbridge found very effective but it is nowadays not available in sufficient amount for general use.

Hutchinson (34) proved that quicklime (CaO) applied without previous slaking, acts as a partial sterilizing agent when used in sufficient amount. In this connection it is interesting to recall Laurent's observation of the stimulation of nitrification due to liming (see p. 36).

Emmerich, Leiningen and Loew (35) found in chloride of lime (bleaching powder) a material which may sometimes be used with advantage as a soil antiseptic. Bleaching powder was reported by Russell and Petherbridge (33) as promising.

The Cyanide Group. Mamelle (36) suggested the injection, as a substitute for carbon disulphide, of solutions of potassium cyanide

into the soil. He claimed that such treatment would be possible, the substance proving toxic to soil pests without injury to the plant. De Ong (37) confirmed this view but found that owing to the variable manner in which hydrogen cyanide was adsorbed by the soil, it was impossible to estimate the dosage required to act upon the soil insect and yet be non-phytocidal.

Calcium cyanide has been found successful against Pear Midge larvæ in New Zealand (38) but its greatest use so far as a soil fumigant is for the control of wireworms, larvæ of the Click Beetles (Elateridæ). Campbell (39) showed that calcium cyanide, though possessing good toxicity against this pest, had to be used in amounts so large that the treatment was too expensive for commercial use. By pre-baiting, the sowing in spaced rows across the field of seeds which by their germination attract the wireworm, the pest could be destroyed by the application of less calcium cyanide.

The field-scale investigation of wireworm control has been handicapped by difficulties of experimental technique such as the determination of the wireworm distribution in the soil. Sampling methods of the type devised by Ladell (40) will facilitate research in the problem but no chemical treatment suitable for the control of wireworm as an agricultural pest has yet emerged, the most promising being the carbon disulphide-naphthalene emulsion used by Miles and Cohen (41).

Search for a suitable soil fungicide for the control of the " damping off " of tomato seedlings led to the introduction of Cheshunt Compound, a mixture of copper sulphate and ammonium carbonate (see p. 133) (42). If the damping-off is due to *Phytophthora* spp., it can be stopped by watering on to the soil around the young plants a dilute solution of this mixture (43).

Attempts have been made, from time to time, to utilize the more potent inorganic sterilizing agents, such as mercuric chloride and copper sulphate, as soil antiseptics. These two fungicides have been suggested in particular for the control of the Potato Wart Disease caused by *Synchytrium endobioticum*. Rivière and Pichard (44) have tested sodium arsenate (Na_2HAsO_4) for the partial sterilization of the soil. Such materials, however, usually fail because of the extreme rapidity with which they are adsorbed by the soil. Hunt, O'Donnell and Marshall (45) found in a general examination of the penetration of soil fungicides, that the addition of salt ($NaCl$) to mercuric chloride greatly improves the penetration of that chemical. Similarly the penetration of copper sulphate solutions

was improved by the addition of sodium chloride. It is noteworthy, however, that these workers found considerable plant injury following the application of such chemicals. It would seem that rapid adsorption by the soil (i.e. poor penetration) is requisite if such materials are not to cause plant injury.

Mercuric chloride was found by Preston (46) to be effective for the control of " Finger-and-toe " of brassicas, caused by *Plasmodiophora brassicæ* Wor. A dilute solution is used to water-in the young cabbage plants when they are transplanted from the seed bed. The method is not only quicker in securing control than liming (see p. 289), but provides protection from the Cabbage Root Fly, *Phorbia brassicæ* Bch. (47, 48), if the treatment is continued at intervals after transplanting.

The intensely poisonous nature of mercuric chloride is a disadvantage which has recently been countered by the extension of Glasgow's recommendation (49) of its substitution by mercurous chloride (Calomel) against certain Diptera infesting vegetable crops. The success of calomel against *Phorbia brassicæ* was recorded by Gasow (50) and by Bourne *et al.* (51) while Dunstan (52) and Wright (53) found it effective against Onion Fly, *Hylemyia antiqua* Mg.

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Effects of Partial Sterilization on Plant Growth.

Of the general soil antiseptics, apart from those materials employed against specific soil pests, heat, cresylic acid, formaldehyde and, to a less general extent, carbon disulphide, are the most important. Cresylic acid is recognized as a soil insecticide of little value as a fungicide ; formaldehyde is inefficient as an insecticide yet of merit as a soil fungicide.

Apart from the direct effect of these antiseptics upon soil pests, there results from partial sterilization certain changes in the microflora and fauna and in the chemical and physical properties of the soil which exert that extraordinary influence upon plant growth which has rendered partial sterilization of such importance.

An early theory, due to Koch (54), suggested that the small amount of antiseptic acts, in a manner similar to that discussed on page 273, as a stimulant to the plant. Such a theory fails, however, to account for the lasting effect of partial sterilization.

In the study of the increased fertility of partially-sterilized soils, attention has been mainly directed to the rapid multiplication of bacteria in the treated soil, first noted by Hiltner and Störmer (55). The general course of events following treatment is a preliminary temporary reduction in bacterial numbers for the first few days with a subsequent rise dependent on the conditions of treatment. According to Russell (56), this increase of bacterial numbers, after drastic treatment, is permanent, but Matthews (57) showed in her trials that there was always a gradual fall back to normal, much slower in field soils than in the richer glasshouse soils.

Hiltner and Störmer advanced, as an explanation of the bacterial increase, the theory that carbon disulphide and other poisons upset the equilibrium of the soil bacteria to the benefit of certain groups. There is a strong suppression of nitrifying organisms. It was observed by Heinze (58) that the nitrate-forming bacteria were depressed by the action of carbon disulphide, and that there is a striking interval of time before nitrification restarts. In addition, Hiltner and Störmer confirmed Gerlach's (59) view that by treatment with carbon disulphide, the denitrifying bacteria are destroyed. It is probable that partial sterilization by heat has a similar result for the non-sporing bacteria will be killed by heat while the spores survive—the ammonifying bacteria are spore formers. The initial fall of bacterial numbers therefore follows from the simplication of the bacterial flora which leaves the survivors free of the competition which, in the untreated soil, limits their numbers.

Russell and Hutchinson (60) advanced the view that this limiting factor was the protozoa of the soil. The status of protozoa as soil organisms had till that time received but little attention, and, as a result of this suggestion, extended observations were made at Rothamsted upon the part played by these organisms. It was found by Cutler (61) that, owing to the adherence of these organisms to the soil particles, the number present in normal soil had previously been underestimated. Daily counts of soil bacteria and soil protozoa revealed an inverse relationship between the numbers; when the bacterial numbers were low the number of trophic amœbæ was high and vice versa. Cutler and Crump (62), regarded this feature as a clear demonstration of the relationship of protozoa and bacteria put forward by Russell and Hutchinson.

Waksman and Starkey (63) were unable to support the protozoa theory except in the case of certain abnormal soils of high moisture and organic matter content of the glasshouse type. These workers held that account should be taken of the part played by soil fungi and Actinomycetes. They suggested that in normal soils much of the decomposition of organic matter is carried out and the products utilized by fungi. After partial sterilization the bacteria are left to carry on this decomposition and as they assimilate less of the carbon and nitrogen, a larger amount of ammonia is produced. They traced a relationship between soil fungi and bacteria similar to that observed by Cutler and Crump between soil protozoa and bacteria.

Other workers have found the assumption of the destruction of a biological limiting factor to be, at least, not essential to account for the increase of bacterial numbers. Not only is there a simplification of the soil flora and fauna to the advantage of the survivors but the material of the organisms killed by the treatment becomes available as food supply for the bacteria. Further, Richter (64) observed in soils, partially sterilized by heat, that though the total nitrogen content was unaltered, there was an increase of readily available nitrogen and a decomposition of the organic matter. Greig Smith (65) suggested that carbon disulphide, when applied to soil, acts as a solvent for the soil wax or " agricere " which normally " waterproofs " the decomposable organic matter. The treatment therefore renders this supply of nutrient available to the surviving bacteria. A new concept was introduced by Matthews (57), who showed that the relative extent of the increase of bacterial numbers in the early days following treatment with the aromatic hydrocarbons, is governed by the toxic chemical employed. The

extent of increase was proportional to the heat of combustion of the chemical used. Matthews therefore concluded that the increase of bacterial numbers is largely due to the feeding value (the energy supplied as given by the heat of combustion) of the antiseptic.

A number of secondary effects of partial sterilization upon the plant are of importance. Considerable work has been carried out upon the observation of Schulze (66) that the development of the plant in soils, partially sterilized by heat, is, in the initial stages of growth, slower than that of plants on the untreated control. Later, however, the plant on the treated soil showed the more luxuriant growth. The temperatures Schulze employed were higher than usual for partial sterilization but Pickering (67) showed that working with temperatures from 60–150° C., there is a retardation of germination in the treated soil which he attributed to the formation of a toxic material, probably a nitrogenous compound. This, however, slowly loses some of its inhibitory properties. Russell and Petherbridge (68) considered the retardation, which they also found in certain cases of partial sterilization of the soil by means of chemicals, due to changes in the soluble soil constituents which, though useful to older plants, are detrimental to the delicate processes of germination.

The secondary effects of partial sterilization are also shown by certain characteristics in the later life of the plant. In plants growing in soils heated to 93° C. Russell and Petherbridge (69) found a remarkable development of fibrous root. The plants had larger leaves of a deeper green colour and usually shorter internodes than the control plants, giving a more compact, vigorous habit. These results were not shown in soils treated with a volatile antiseptic, but in all cases it was observed that the roots and stems give up their nitrogen, phosphorus and potash more completely to the fruit. As a result the quality of the fruit, at least in the case of cucumber and tomato, was superior to that from the untreated soil.

Finally, in the case of leguminous plants (which differ from others in that to take up their nitrogen they enter into a symbiotic relationship with certain nitrogen-fixing bacteria), to secure a satisfactory crop after partial sterilization it is generally necessary to re-inoculate the treated soil with the proper bacteria.

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SOIL CONDITIONS AND THE PEST

Next for consideration come the methods by which the soil conditions are rendered less favourable for the pest (see p. 40). This question has been regarded mainly, so far, from the aspect of soil acidity or, better, the intensity of this acidity, i.e. the hydrogen ion concentration of the soil. Plants are tolerant to certain ranges of hydrogen ion concentration of the soil. The extent of this range varies with general conditions and with the species of plant, but for the majority it includes that corresponding to the neutral point. In a similar manner, disease organisms and animal pests have their characteristic tolerated range of pH. If now the tolerated range of host plant and pest do not coincide, it is possible to adjust the hydrogen ion concentration of the soil, rendering it favourable for the plant and unfavourable for the pest.

One of the earliest examples of this type of control is due to Halstead (70), who found that liming eradicated club-root of turnip. It is now known that the organism concerned, *Plasmodiophora brassicœ*, producing the " Finger-and-toe " or Club-root of many brassicas, thrives in a soil more acid than is most suitable for this type of plant. By liming the soil the acidity is reduced, improving the soil for the crop and rendering it less suitable for the fungus.

To take an example at the other end of the scale, Halstead found that the application of sulphur as a fertilizer reduced the amount of Scab on potatoes. Gillespie and Hurst (71) found that the distri-

bution of Scab, due to *Actinomyces scabies*, was closely related to the reaction of the soil. The disease was rare on acid soils of pH below 5·2, but was common on soils of pH above 5·2. It is for this reason presumably that liming is regarded with caution among potato growers, for the decrease of soil acidity which it brings about will favour Scab. Cultural and manurial measures resulting in an increase of soil acidity may then be regarded as control measures against this pest. The success of sulphur, used as suggested by Halstead, is now thought to depend upon the increase of soil acidity it brings about. A series of papers by American investigators (72) reported favourably on the efficiency of sulphur in this respect and it is considered that the control arises from the oxidation of the sulphur to sulphuric acid, for not only are the more finely-divided sulphurs more effective but improvements were obtained by inoculating the soil with sulphur bacteria (e.g. *Thiobacillus thiooxydans*), thereby aiding the oxidation processes.

A second method of rapidly increasing the soil acidity is by green manuring, the ploughing in or application of green vegetable matter, a practice found by Millard (73) to inhibit Scab of Potatoes, Sanford (74), however, did not obtain favourable results by this method. Millard and Taylor (75) have introduced a biological theory of the action of green manuring, a theory discussed under Biological Control (p. 64).

The application of sulphur to the soil was also found to effect a reduction of the Wart Disease of Potato (*Synchytrium endobioticum*) by Roach, Glynne, Brierley and Crowther (76). The disease was not, however, entirely eradicated and it was found that its elimination was not solely a matter of increasing the soil acidity. Further, as no increased efficiency could be obtained by the inoculation of the sulphur with *Thiobacillus thiooxydans*, it was concluded that the active fungicidal agent is not the hydrogen ion but is some sulphur compound other than sulphuric acid. Roach and Glynne (77), studying the toxic action on winter sporangia of *S. endobioticum* of various sulphur acids likely to be formed when sulphur is added to soil, found that acidified solutions of sodium thiosulphate, sodium hydrosulphite and sodium formaldehyde sulphoxylate were about ten times as toxic as sulphuric acid. In view of the generally-held view that acidified solutions of these compounds are highly unstable, Roach (78) investigated their degree of stability and concluded that the formation of thiosulphuric acid is the probable cause of the fungicidal action of sulphur on *S. endobioticum*.

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MECHANICAL METHODS

Of the mechanical methods of soil treatment, the most obvious when dealing with small areas of soil such as seed-beds and glass-house soils, is to discard the infected soil, replacing it by soil free from pests or disease organisms. This method suffers from many disadvantages. Firstly, there is the wastage caused by discarding a soil, often richer in plant foods than average farmyard manure and the necessity of supplying the fresh soil with these nutrients. Secondly, there comes the difficulty of securing a suitable supply of uninfected soil and its storage, and, finally, the danger of rein-fection of the new soil from the subsoil left in the glasshouse and from the old soil remaining on walls, pipes, tools, wheelbarrows and the workmen's boots.

The processes of cultivation such as ploughing and hoeing are frequently of great importance in the control of soil pests. Seasonal ploughing exposes the larvæ and pupæ of soil insects to birds and other animals or it may effect their burial. For example, as the European Elm Sawfly Leaf-miner (*Kaliosysphinga ulmi* Sund.) pupates within one inch of the soil surface, Chrystal (79) recommended the removal and burial at a depth of below six inches of a thin layer of soil from beneath the tree. Theobald (80) after trials with various chemicals for the control of an exceptional plague of cockchafer larvæ, found that rolling the affected area by means of a steam roller was effective. The practice of " Sub-mergence," drowning the pests by flooding the soil for a suitable length of time at the suitable period, has already been dealt with on page 42.

Of greater interest is the method generally known as " Crop Rota-tion." The rotation of crops is the old-established device of growing a succession of crops on the same land, which brings great advan-

tages to the grower. These advantages, briefly, are saving of manure, better utilization of the nutrient resources of the soil, an economical distribution of labour and finally, crops of greater vigour. This last advantage is due, among other reasons, to the fact that if the same crop be grown on the same land continuously it is more liable to be attacked by pests. Continuous cropping like-wise leads to the accumulation of the particular weeds of the crop, hence crop rotation forms a valuable method of weed control.

Considered solely as a method of pest control, crop rotation involves knowledge of the life history and habits of the pests to be eradicated. The pest must not be capable of over-wintering for more seasons than the period of the rotation, nor should that rotation include any crops which would serve as host plants for the organism.

These requirements may present difficulties, for instance, *Plasmo-diophora brassicæ*, the organism causing Club-Foot of cruciferous plants, has been known to live in the soil up to six years. A six-year rotation containing no cruciferous crop would therefore be necessary to secure its destruction by crop rotation. Further, it would be necessary to remove all weeds able to serve as host plants.

Crop rotation, as a method of pest control, is limited to annual crops and economic conditions do not always warrant its use. The method is frequently impracticable in the intensive cultivation of market garden and glasshouse crops, where the range of crops sufficiently profitable to grow is limited. The method is applicable only to organisms whose migration by other means cannot be controlled and it is necessary to prevent re-contamination of the treated soil by infected manure, seed, or by drainage water from infected land.

The method is of value when conditions are favourable, as may be shown by the following examples. Leukel (81) showed that " Purples," a wheat disease caused by the nematode *Anguillulina tritici*, can be eradicated from infested land by growing a non-susceptible crop for two or three years. Shaw (82) found crop rotation the only practicable method of controlling the sugar-beet nematode, *Heterodera schachtii*, on large areas. Using crops not susceptible to the pest, a rotation of five to six years was necessary because of the persistence of the " brown cyst " stage of the eel-worm. The long viability of the cysts is a serious disadvantage of the method. This may be removed if there is a successful out-come of the investigations resulting from the observation of Baun-

acke (83), that the emergence of larvæ from the cysts is stimulated by root excretions from susceptible plants. Trifitt (84) confirmed the observation for the potato strain of the eelworm and observed that the stimulant substance excreted from the roots of growing potato plants is active only in the presence of oxygen, is non-volatile and, to some extent, thermostable. A substance of similar properties was found in the root excretions of certain grasses whereas mustard plants were found to give off a substance which checks cyst formation of *H. schachtii* on the roots of potato.

The proof of the excretion of stimulant products from the roots of plants susceptible to the eelworm provides a new principle for the control of *H. schachtii*. It might, for example, be possible to break the resting period by stimulating the emergence of the more easily controlled larvæ from the resistant cysts. Triffitt (85) reported preliminary observations of the effect of a selected grass leys upon the viable cyst population of a potato-sick soil. Alternatively, chemicals such as bleaching powder (86) and other hypochlorites (87) might be used to stimulate emergence. The possibility of adding to the soil chemicals which tend to neutralize the larvæ-liberating principles of the potato root excretion is also being studied by Hurst and Triffitt (88). Laboratory experiments, by Smedley (89), indicated that the simpler chloro-acetates might be of value but the field trials of O'Brien *et al.* (90) and of Edwards (91) showed that, though the yield of potatoes was improved by the application of calcium chloro-acetate, $Ca(CH_2Cl.COO)_2$, to eelworm-infested soil, the cyst numbers were not reduced.

A modification of the principle of Crop Rotation is used to combat wireworm on newly-ploughed grassland. By taking a crop suscep-tible to wireworm, e.g., potatoes, in the first year of the ploughing-up, severe injury may be avoided because of the presence of ample alternative food for the wireworm in the ploughed-in turf. If grown in the second year, the potato crop might suffer severely as shown by Miles and Cohen (92) whereas a wheat crop, if of a freely-tillering variety, might grow away from the wireworms' attack.

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CHAPTER XIV

TOXIC ACTION AND CHEMICAL CONSTITUTION

THE MEASUREMENT OF DEGREE OF TOXICITY

When you can measure what you are speaking about, and express it in numbers, you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind :

Thomson, W., *Popular Lectures and Addresses.*
London, 1889. Vol. I, p. 73.

Measurement is a process of comparison and only by the use of methods of comparing the value of the various chemicals used as insecticides, as fungicides, as seed disinfectants or as soil partial sterilizing agents, can the full benefit of the application of chemistry to Plant Protection be secured.

The acid test of any insecticide or fungicide is its performance under practical conditions, and field trial is the ultimate criterion. But the comparison of insecticides or fungicides by the method of field trial is an expensive, laborious and lengthy process ; expensive for the provision of adequate biological material is necessary, laborious because of the work involved in obtaining quantitative results, lengthy because repetition in order to obtain a sufficient variation in environmental factors is required to justify a generalization applicable to average conditions. It is, in fact, advantageous to obtain, in the series of field trials, the maximum variation of the many factors such as degree of infestation, variations in the variety and condition of the host plant, in climatic conditions and in methods of application, which affect the performance of the insecticide or fungicide, for the greater the extent of these variations, the more generally applicable will be the result of the comparison.

Progress by the method of field trial is so slow that many attempts have been made to simplify, by analysis, the method. The influence of one or more of the variable factors is eliminated and, by the combination of the results of a series of trials in which different variables have been held constant, an attempt is made to synthesize a comparison which will hold good under field conditions. This

analytical procedure is the principle of the method of laboratory trial.

To illustrate the application of the method of laboratory trial as a means of assessing efficiency, the comparison of two arsenical stomach poisons may be analysed upon the following broad lines. Firstly, the relative toxicity of the two products may be compared using a series of leaf-eating larvæ as test organisms ; secondly, the phytocidal properties of the two products may be compared upon representative types of foliage ; thirdly, the retention and tenacity of the two materials upon specific surfaces may be determined. A combination of the results of these tests would, perhaps, suffice to enable a generalization to be made upon the relative efficiencies of the two products as stomach insecticides.

But if the comparison of the inherent toxicity of the two poisons is required to permit, for example, the correlation of toxicity with chemical structure, a further analysis of the results of the biological assay is required. The relative efficiency of each substance in the biological test, i.e. the insecticidal or fungicidal value, is determined not only by inherent toxicity, but by physical factors such as particle size, degree of dispersion, availability or solubility. Thus a suspension of rotenone crystals would prove less toxic than one in which the rotenone, at the same concentration, was maintained in a high state of dispersion in the presence of resins inhibiting crystallization. The influence of physical condition is illustrated in the studies of the fungicidal value of cuprous oxides by Horsfall and his colleagues (1).

It will be seen that the determination of the degree of toxicity to insect or fungus is but one item of the assessment of insecticidal or fungicidal efficiency. It is, nevertheless, of such importance that, within recent years, it has been extensively investigated (see 2, 3). It has been found that the observance of certain general rules is, if not essential, conducive to the attainment of concordant and satisfactory results. The primary purpose of these rules is, by the elimination of variation in the experimental conditions, to enable significant results to be obtained with the minimum of replication.

In the first place, the test organism should be standardized, for, by eliminating variations in the resistance of the organisms to the toxic substance, results of sufficient uniformity can be obtained with the minimum number of organisms. Thus, in the determination of the ability of a protective fungicide to prevent spore germination, spores of a similar age should be used. For the evaluation of

stomach poisons, Campbell and Filmer (4) used silkworms of the same instar.   In their studies upon contact insecticides, Tattersfield and his colleagues (5) employed only alienicolæ of one generation reared from a single fundatrix of *Aphis rumicis*.   For the comparison of direct fungicidal properties upon the Hop Powdery Mildew, a difficulty arises, for no means are yet known for the culture of such a highly-specialized fungus on artificial media.   Salmon (6) overcame the difficulty by using only hops propagated vegetatively from one parent clone plant, selecting for treatment, leaves and mildew patches in the same stage of active growth.   A similar precaution was described by Staudermann (7) using *Plasmopara viticola* as test organism.   To simplify the rearing of suitable numbers of test organisms a selection of the more easily-handled species is often possible.   The requirements of insects suitable for routine testing are discussed by Steer (8) and by Craufurd-Benson (9).

In the second place the test organism must be exposed to a known concentration of toxic material applied in a standardized manner. For the examination of direct insecticides or fungicides which, in practice, are applied in a medium completely wetting the surfaces involved, uniformity of application may easily be obtained by an immersion or dipping method.   This method is well suited for the testing of ovicides using insect eggs laid on bark or other easily-wetted surfaces (10) but, for insects in active stages, Tattersfield (11) considered that there was a danger of stomach poison effects being added to the contact action, a risk which Craufurd-Benson (12) accepted because of the greater convenience of the method over spraying.   Of spraying methods the simplest is that used by Salmon (6) who, using sprays of good wetting properties, found that application continued until the Powdery Mildew was thoroughly wetted gave concordant results.   This method would fail to give equal spray loads with sprays of different and inferior wetting properties (13) with which a constant deposit is obtained by spraying a surface of standard wetting properties held at right angles to the axis of the spray cone with a constant amount of spray under constant conditions, the amount selected being below the point of run-off for all the sprays used.   This principle was used by Marsh (14) and is the basis of the more elaborate apparatus devised by Tattersfield and Morris and calibrated by Tattersfield (15).   The various methods adopted to obtain constant spray or dust deposits of insecticides are surveyed by Tattersfield (2), but mention may be made of the methods used by Montgomery and Moore (3) for the

application of measured amounts of protective fungicides to known areas. The direct application of the toxic insecticide by means of a micropipette was used by O'Kane (16) and by Nelson (17) and their colleagues, but this method is better suited to the examination of the site of action on the insect body than to the routine testing of insecticides.

In the third place, environmental factors should be held constant, as a general rule, at the optimum condition for the growth of the organisms or for the establishment of infection. The laboratory method for the comparison of fungicidal efficiencies against Apple Scab (*Venturia inæqualis*), devised by Keitt and Jones (18) and used by Hamilton (19), affords an example of the latter case. The effect of variation in soil moisture on the relative fungicidal efficiencies of seed disinfectants in the control of *Helminthosporium avenæ* are shown in Muskett's work (20). The biological assay thus requires not only a thorough knowledge of the influence of environmental factors in the growth of the test organism and of the epidemiology of the disease or infestation, but a knowledge of the effect of these factors on the response of the organism to toxic substances. The influence of pre-history on the response of the beetle, *Ahasversus advena* Waltl, to rotenone-containing sprays is well described by Craufurd-Benson (9).

Finally, there should be uniformity in the method of recording results and deducing a figure representing toxicity. In some cases, suitable methods are obvious ; in tests of ovicides, for example, the proportion of eggs hatched to total eggs may be taken if it is known that the proportion of viable eggs per test is constant. Salmon accepted the minimum concentration of toxic constituent necessary to prevent the regrowth of conidiophores within ten days after treatment, a period long enough to indicate the death of the mycelium, as the index of direct fungicidal properties. In other cases, complications arise, as in spore germination tests when there may be germinated spores of which the germ tubes show abnormalities suggestive of a toxic action ; a figure based upon the proportion of spores germinated to total spores will not reflect this type of toxic action. Further, the effect of the material under test may not be to inhibit germination but to extend the latent period before germination, a phenomenon clearly shown in Tomkins' experiments (21). Adequate measures must be taken to ensure that a retardation of germination is not interpreted as non-germination, although, in actual practice, a fungistatic action may achieve the same purpose

as a fungicidal action.   In insecticide tests, complications may arise
through the difficulty of determining precisely the death or time
of death of the insect.   Campbell (22) examined the effect of the
substitution of " knock-out " point for death point, defining " knock-
out " as the inability of the silkworm to regain its feet after being
pushed over, and death as the absence of response to touch.   He
showed that the relative toxicities of lead hydrogen arsenate and
sodium silicofluoride depended on the choice of end-point, but he
regarded the " knock-out " point as the more practical because it is
more easily determined.   Richardson (23) also employed paralysis
as an index of toxicity, comparing the results with the proportion
of dead and live flies after a suitable interval.   He selected paralysis
by reason of its greater sensitiveness in determining differences in
relative toxicity.   Tattersfield (24) directed attention to the need
for observations of the ultimate effect of the insecticide, for, with
the pyrethrins, for example, narcosis rapidly follows treatment and
recovery may occur with sub-lethal doses.   Tattersfield and his
colleagues (5) have successfully used the percentage of moribund
and dead insects as the criterion of insecticidal properties of contact
insecticides.

By such methods of recording, a series of mortality figures,
based upon the proportion of affected to total organisms or upon
the time of survival of the organisms, for different concentrations
of the active substances under test is obtained.   When plotted on
squared paper, a mortality-concentration curve is obtained which
is generally of a sigmoid character.   The sigmoid nature of the
curve, as Henderson Smith (25) pointed out, may be explained by
the assumption that it reflects variations in susceptibility between
individual organisms.   As, at a given concentration, the mortality
figure includes those individuals susceptible to lower concentrations,
the curve may be regarded as an integrated or cumulative normal
frequency curve.   Upon this assumption, complications due to
variations in the relative susceptibilities of individual organisms
should be removed if the mortality-concentration figures are plotted
upon arithmetic probability paper or by the conversion of the mor-
tality percentage to the corresponding " probit," a statistical unit
devised by Bliss (26).   Each procedure has been found to reveal
either a straight-line or logarithmic relationship between mortality
and concentration.   Henderson Smith (27), for example, found
that, on plotting the logarithm of the time taken to kill 50 per
cent. of the *Botrytis* spores by heat against the reciprocal of the

temperature, his points fell on a straight line. O'Kane and his co-workers (28) showed that, by plotting upon logarithmic papers the mortality data of Tattersfield and Gimingham of the toxicity of nicotine-saponin solutions to *A. rumicis*, corrected by the use of probability paper, a straight line was obtained.

The successful transformation of toxicity data to a linear relationship has had valuable corollaries. It permits the calculation of the statistical significance of the results and justifies, with certain qualifications, the use of a single figure to represent toxicity. For comparative work the most convenient value is the concentration corresponding to 50 per cent. mortality, termed by Trevan (29) the " median lethal dose." For practical purposes knowledge of the relative toxicities at concentrations giving the theoretically-unobtainable 100 per cent. control is required and may be determined by methods described by Bliss (30). Apart from these statistical advantages, the method throws light on the mechanism of toxic action and the significance of the linear or logarithmic relationship is discussed in the next section. It has been found, however, that, over the whole range of concentration, the mortality points do not always fall on one straight line but show, usually at the lower concentration, a change of slope (see e.g. 26). As the explanation of such " breaks " in the toxicity curve cannot be non-uniformity among the organisms tested it rests in heterogenity in the toxic material used. Perhaps, at the low dilutions, the toxic substance is not presented to the organism in the same physical form as at higher concentrations ; perhaps the toxic material is itself non-uniform, and contains more than one toxic constituent. The latter possibility has been examined by Bliss (31), who showed that the type of curve provides evidence of the types of joint action possible when organisms are exposed to poisons containing more than one toxic constituent. These types are :

(1) Independent joint action, when the constituents act independently and diversely ;

(2) similar joint action, when the constituents act independently but similarly ;

(3) synergistic action, when the toxicity of the mixture is greater than that predicted from studies of the individual constituents. This process is the reverse of antagonism and offers a promising field for development now that a method for the precise evaluation of the degree of synergy is available.

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THE RELATIONSHIPS OF CHEMICAL CONSTITUTION AND TOXICITY

Life is so complex a process that it is obvious from the outset that any attempt to correlate the chemical constitution of a toxic material and its toxicological action must be incomplete and hypo-

thetical in nature. The study of the toxic action of insecticides and fungicides is but one of a number of related physiological problems ranging from germicidal action on bacteria to narcotic action on man. Although there are unexplained points of difference between the toxic action of a chemical upon different organisms, a number of striking general features of toxic action must be mentioned.

One point in common throughout the whole plant and animal world is the structural unit, the cell. Not that all cells are alike in character but that every organism is composed of one or more such units. The cell may be the apparently structureless amœba or it may be one of the highly specialized organism known as man, but in both cases it may be regarded as a mass of protoplasm surrounded by a more or less well-defined boundary or membrane. This cell membrane, or better, plasma membrane, may be independent of the cell wall, a feature of much importance in the plant world, and is regarded merely as the limiting boundary of the cell protoplasm. It is in dealing with the behaviour of this plasma membrane that glimpses have been obtained of the complicated physico-chemical interactions occurring within the living cell.

In the discussion, in the previous section, of the relationships between the mortality figures and concentration of the toxic substance, it was mentioned that, after correction for variations in individual susceptibility by transformation to probits or by plotting on arithmetic probability paper, the curve mortality/concentration is frequently logarithmic in character. It would appear therefore that the actual amount of toxic substance involved in toxic action is not always a linear function of the total amount of poison available but is a logarithmic function analogous to that involved in an adsorption process. That toxic action is associated with adsorption phenomena is an hypothesis which has been frequently used and tested in biology (see e.g. 1) and which was first applied to insecticidal action by O'Kane and his colleagues (2).

As adsorption presumably occurs at the interface of the plasma membrane and the solution carrying the toxic substance, an association may be expected between the toxicity and the adsorption of surface-active materials, the use of which as spreaders and emulsifying agents has already been discussed (pp. 81 et seq.). Surface adsorption at the interface solution/air is indicated when the surface tension of the solution is lower than that of the solvent. Further, by taking the reciprocal of the equivalent concentration necessary

to lower surface tension by a fixed amount, a figure representing the surface activity of the substance, the specific surface activity, may be deduced. It has been shown that with a series of related organic compounds, e.g., an homologous series, the specific surface activity frequently exhibits a regular increase as the series is ascended. This generalization, known as Traube's Rule, may be expressed thus : that, whereas the molecular weights of an homologous series ascend in arithmetic progression, the specific surface activities form a geometric progression. This geometric progression was shown by Traube (3) to be of the ratio $1 : 3 : 3^2$: in the fatty alcohols and alkyl acetates ; that of the fatty acids examined by Traube, Szyszkowski (4) and Forch (5) to be approximately $1 : 3 : 3^2 : 3^3 : \ldots$

A numerical ratio of the same type has been shown to exist in the relative toxicities of certain members of homologous series. For instance, Fühner (6), in an investigation of the narcotic action of the light petroleums upon rats and mice, showed that in the series of normal paraffins, pentane C_5H_{12} to octane C_8H_{18}, each member is three times as active as its lower homologue. Uppal (7), investigating the toxicity of the alcohols towards the spores of *Phytophthora colocasiæ* Rac., found that the equivalent toxicities of ethyl alcohol C_2H_5OH, normal propyl alcohol C_3H_7OH, and normal butyl alcohol C_4H_9OH were in the ratio of $1 : 3 : 3^2 : \ldots$; agreeing with the discovery of Kamm (whom he quotes) that the molecular toxicity of various normal primary alcohols upon Paramecia (species of Protozoa) ascended with the homologous series in the same geometric progression.

It is not to be expected that so regular and simple a relationship will hold for all examples of the toxicity of members of an homologous series. In the first place, Traube's Rule was based upon the properties of the solution/air interface ; toxicity is concerned with the membrane/solution interface. Freundlich (8) was able, however, to quote examples, where Traube's Rule was applicable, of systems in which the second phase was gas, liquid or solid. Secondly, in not every case can the common ratio be expected to be three ; Stiles and Stirk (9) found that the average ratio for the surface tensions of aqueous solutions of eight homologous alcohols was 3·3, whereas that for the toxicities of the alcohols was somewhat lower. Further, the rule can only hold when each additional —CH_2— group comes into play in the same manner as with each previous member of the series. This is conceivable only when the

mode of orientation of the molecules at the interface is similar throughout the series. There will presumably come a point when the addition of another $-CH_2-$ group will upset the equilibrium. In such cases the toxicity of the series may be expected to increase rapidly with molecular weight until a point is reached when the addition of the $-CH_2-$ group will cause a less marked increase, or perhaps a decrease, in toxicity.

The increase of activity with rise of molecular weight of an homologous series has been frequently encountered in the foregoing pages and, in some cases, activity has been found to decrease when the molecular weight rises above a certain point, an inflexion which has been ascribed to the intervention of other factors. On page 84 the increase of activity of the sulphated alcohols with molecular weight is described, the inflexion being attributed to solubility factors. On page 154 the increase of fungicidal properties of certain types of dye-stuff with molecular weight is recorded, the inflexion being ascribed to the inability of large molecules to pass through the cell wall. The example of the insecticidal properties of the soaps (p. 214) has been discussed from the viewpoint of the Lipoid Theory, whilst an outstanding case is the relationship between the molecular weight and toxicity of the alkyl thiocyanates (p. 222).*

As surface activity in the homologous series rises, the tendency of the substance to go into solution decreases, an observation which is the basis of Traube's " Haftdrück " theory. Expressed in another form, the addition of each $-CH_2-$ group augments the non-polar character of the molecule, rendering it less water-soluble but increasingly soluble in non-polar solvents such as hydrocarbons and oils. It would therefore be expected that the partition coefficient † oil/water will increase as the homologous series is ascended. Traube (10) showed that the partition coefficients in the systems benzene/

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* The toxicity relationships of the homologous series have been strikingly demonstrated and utilized in the field of antiseptics and chemotherapy. The interested reader is referred to the work of Dohme, A. R. L., Cox, E. H. and Miller, A., *J. Amer. chem. Soc.*, 1926, **48**, 1688 ; of Coulthard, C. E., Marshall, J. and Pyman, F. L., *J. chem. Soc.*, 1930, 280 ; Coulthard, C. E., Levene, H. H. L. and Pyman, F. L., *Biochem. J.*, 1933, **27**, 727 ; **28**, 264; and of Black, R., Shaw, H. and Walker, T. K., *J. chem. Soc.*, 1931, 272.

† If a solution of a substance be shaken with a second liquid, immiscible with the first liquid and in which the substance is also soluble, the relative concentration of the substance in the two layers, i.e. c_1/c_2, will, provided there is no change in the molecular state of the substance, be constant. This figure c_1/c_2 is the " partition coefficient."

water, carbon disulphide/water and carbon tetrachloride/water of methyl, ethyl and propyl alcohols were approximately in the ratio 1 : 3 : 3². That toxicity is related to the relative solubility of the substance in oil and water was an hypothesis originally advanced by Overton (11) and by Meyer (12), who suggested that, as fatty compounds will be accumulated at the plasma membrane, narcotic action will be governed by the solubility of the narcotic in such fatty bodies. As they named the fatty bodies lipoids, their suggestion is known as the Lipoid Theory. The application of the Lipoid Theory to the toxicity relationships of the fatty acids and of the mercury seed disinfectants has been discussed (see p. 215 and p. 272).

Examples of correlations between toxicity and such factors as surface activity and solubility, are to be found outside the homologous series. For example, the relative toxicities of *ortho-*, *meta-* and *para*-nitrophenol may be taken. Plantefol (13) showed that against the fungus *Aspergillus niger* the *p*-derivative is more toxic than the *o*-derivative. Tattersfield, Gimingham and Morris (14) found that *p*-nitrophenol is a more efficient contact insecticide towards *A. rumicis* than the *o*-compound. Rideal (15) stated that of the nitrophenols the *p*-compound possessed the greatest molar germicidal activity, correlating this activity with the action of the compounds upon the surface tension of water.

With the hydroxyl derivatives of benzene, Cooper (16) showed that the introduction of hydroxyl groups decreased the bactericidal powers of phenol. Tattersfield (17) found that the toxicities of these compounds towards *A. rumicis* is in the same order :

OH ⬡ Phenol	>	OH ⬡OH Catechol	>	OH ⬡OH OH Pyrogallol
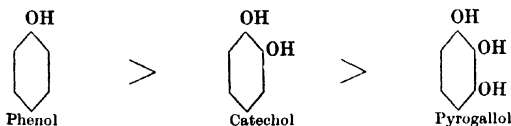
observing that the other dihydroxybenzenes, i.e., resorcinol and

OH ⬡OH Resorcinol	OH ⬡ OH Hydroquinone
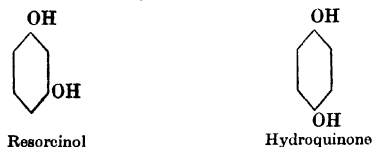
hydroquinone, are also less toxic than phenol. This reduction of toxicity was shown by Tattersfield to run parallel to an increase in the solubility of these compounds in water and, more particularly,

to the increase in the partition coefficients of these compounds between water and benzene.   At 25° C., the partition coefficients water/benzene were :

Phenol, 0·408 ;   Catechol, 9·174 ;   Pyrogallol 125.

Rideal traced a similar relationship between the surface-tension depressant action and germicidal activity of these hydroxy-derivatives, which both run in the order :

Phenol > Resorcinol > Hydroquinone > Pyrogallol.

Brown and Tinker (18) found that barley grains absorbed equi-molecular solutions of different phenols in the order :

Phenol < Catechol < Resorcinol < Pyrogallol,

the latter entering at the same rate as water.

The latter examples of the hydroxy-benzenes suggest that the introduction of additional hydroxyl groups, by increasing the affinity of the compounds for water, has the reverse effect of the addition of the —CH$_2$— group in the homologous series.   Such considerations would not, however, explain the high degree of specificity shown, for example, by the pyrethrins or by rotenone.   These compounds, although highly toxic to certain insects, are but slightly toxic to other organisms, whilst the slight change in structure induced, for instance, by oxidation markedly reduces their insecticidal properties.

Yet an explanation of specificity of both these types becomes apparent on further examination of the thesis of adsorption and orientation at the interface.   Orientation will confer on the interface a definite pattern in which will be distributed certain chemically-active receptor groups, contributed by the organism and arranged in ordered fashion peculiar to that organism.   Similarly the toxicant will contribute active groups to the interface.   If the special distribution of these active groups on the molecular framework of the toxicant fits that of the receptor groups of the organism, combination by intermolecular forces or by secondary valencies will occur, with consequent interference with the vital processes.   The extent of this interference—toxicity—will be determined by the degree of fit.

The importance of molecular structure in relation to toxicity may be illustrated by the example of nicotine and related alkaloids. The nicotine of commerce is the lævo-rotatory form of β-nicotine, 3-(1-methyl-2-pyrollidyl) pyridine, a two-ring structure (Formula I, p. 307).   It would seem that attachment of the two rings in the 3-2

position is a factor determining toxicity, for α-derivatives (Formula II, below), in which the linkage is in the 2–2 position, are less toxic than the corresponding β-compounds (in the 3–2 derivative) as shown in Table I, taken from the results of Richardson, Craig and

Compound.	M.L.D. (mg. per 100 ml.)
dl-β-nicotine	96
dl-β-nornicotine	45
dl-α-nicotine	1496
dl-α-nornicotine	1514
l-β-nicotine	49
Anabasine	5

Hansberry (19). A similar result was obtained by Smith, Richardson and Shepard (20) with certain dipyridyls and piperidyl-pyridines among which the αβ- or βα-derivatives (having the 2–3 linkage) were more toxic than those with the linkage in other positions. The 3-(2-piperidyl) pyridine has been named neonicotine (Formula III, p. 308), and is the inactive form of Anabasine. Table I shows that anabasine is more toxic than *l*-β-nicotine, an indication either that the framework of two six-membered rings is capable of greater toxicity than that of the nicotine frame or that the attachment of the methyl group to the pyrollidine nitrogen reduces toxicity. Considering first the character of the framework, toxicity appears to be related to the saturation of the second ring, for Richardson and Shepard (21) found that nicotyrine (Formula VI, p. 308), 3-(1-methyl-2-pyrryl) pyridine, in which both rings are unsaturated, was from seven to ten times less toxic than nicotine. The same investigators showed that rupture of the second ring, as in metanicotine (Formula V, p. 308), reduced toxicity. The influence

β-Nicotine
(I)

α-Nicotine
(II)

CH₂
/\
CH₂   CH₂
CH | |
CH   C—CH   CH₂
‖ | \
CH   CH   N
\\ // |
N   H

Anabasine
(Neonicotine)
(III)

CH₂—CH₂
| |
CH   CH   CH₂
CH C----CH   \
‖ | N
CH   CH |
\\ //   H
N

β-Nornicotine

(IV)

CH—CH₂
‖ |
CH   C—CH   CH₂
CH | \
‖ | NH
CH   CH |
\\ //   CH₃
N

Metanicotine
(V)

CH—CH
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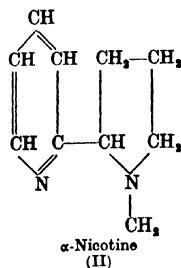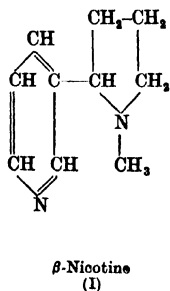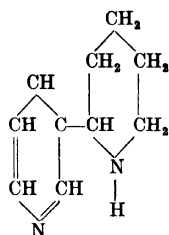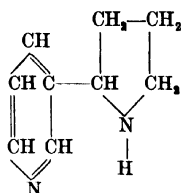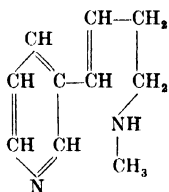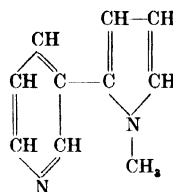
Nicotyrine
(VI)

of the methyl group attached to the nitrogen of the ring is shown by the comparison of the median lethal dose of *dl-β*-nornicotine (Formula IV, above), with that of the corresponding nicotine derivative (Table I). The former has no substituent methyl group and its greater toxicity indicates that the methyl group is not essential for and is probably detrimental to the toxicity of nicotine. An analogous example is recorded by Campbell, Sullivan and Smith (22), who found that N-methyl anabasine was less toxic to mosquito larvæ than anabasine. That the relative spatial distribution of the ring and groups is of great importance in determining toxicity is well shown by the comparison of the median lethal doses of the lævo-rotatory (*l*-) and racemic (*dl*-) forms of nicotine. Indeed the fact that the racemic form is but half as toxic as the lævo-rotatory form suggests that the lævo-fraction is largely responsible for the toxicity of racemic nicotine. The inference is that the dextro-rotatory form is practically non-toxic, yet the only difference in structure between the dextro- and lævo-rotatory forms is that one is the mirror-image of the other. As differences in toxicity among other optical isomers have long been known, and as abundant evidence of orientation at the interface is available from X-ray and physico-chemical investigations, it may be accepted that the physiological properties of the more complex

organic compounds are associated with certain structural frameworks and the distribution and nature of the active groups attached to that framework. The helpful analogy of lock and key suggested by Fischer is thus transformed to a multipoint action which goes far in explaining the specificity shown in many other biochemical reactions * and possibly the specificity displayed in the physiology of parasitism among phytopathogens.

It may then be claimed that the apparently hopeless task of the correlation of the chemical constitution—upon which are dependent physical properties—and the degree of toxicity has yielded most interesting results. The hypotheses advanced are justified if they permit a single sound generalization of service in co-ordinating the isolated and apparently unrelated observations concerning the mode of toxic action of insecticides and fungicides discussed in foregoing chapters. By means of such generalizations, chemotherapeutics has advanced to its present importance. Without them, and without the fundamental work and reasoned imagination which breed and test the hypotheses which lead to such generalizations, chemistry cannot be expected to contribute, in full and useful measure, to the problems of Plant Protection.

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TRAPS

The successful rat-catcher, gamekeeper or angler is he who knows well the behaviour of his prey, its response to changes of external conditions. So, in pest control, the successful application of control methods is dependent on a sound and accurate knowledge of the response of the pest to external stimuli.

The higher animals, especially man, have developed the faculty of controlling the response to external stimuli by memory. There is an ability to choose, the choice being ruled by previous experience and the memory of that experience. In the lower animals and plants, this power of choice is not developed and it is possible to predict the response of such an organism to tropic stimuli. The trapping of these lower organisms should be simpler than the task of the gamekeeper or rat-catcher. The rat may or may not respond to the attractive stimulus of the smell of cheese, but the moth is unable to resist the attractive stimulus of the light of a candle.

But, apart from the work of a few enthusiasts, the scientific study of behaviour among insects is meagre, and little is yet known of their tropic responses. The application of this knowledge to pest control is therefore limited, but its possibilities are indicated by the following examples.

The Aphididæ or Plant Lice are highly specialized suctorial insects with complex life histories, the dependence of which upon external conditions has aroused much interest. *Aphis fabæ* Scop.,* a common polyphagous insect is found in the autumn on a limited number of plants, notably the Spindle tree *Euonymus europœus*. In the spring, however, it leaves this host to invade a wide variety of plants, such as the poppy, mangold, bean, etc. Its life history has been worked out and the following sequence is shown :

(1) The *Fundatrices* or Stem-mothers, wingless females emerging in spring from the overwintered eggs on Euonymus. These females

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* This insect was previously known as *A. rumicis* L., a name now confined to a non-migratory form which lives on the Dock (*Rumex* spp.).

possess that remarkable power among insects of producing young, born as miniatures of their parent. The mother is said to be " viviparous " as distinct from the more usual egg-laying or " oviparous " female insect. Further, for this act of reproduction the previous intervention of the male is unnecessary, a phenomenon known as " parthenogenesis." The *Fundatrices* are therefore wingless, viviparous, parthenogenetic females which produce the—

(2) *Fundatrigeniæ*, likewise (usually) wingless, viviparous, parthenogenetic females which live on the primary host. After the first or second generation, however, there appear the—

(3) *Migrantes*, which differ from their parent in being winged. It is at this stage that migration to the secondary host, the bean, etc., occurs. Here are next produced the—

(4) *Alienicolæ*, again parthenogenetic viviparous wingless females of extraordinary fecundity, the young reproducing so rapidly after birth— in nine to twenty days—that enormous numbers of aphides are produced in the summer. Successive generations of the *Alienicolæ* are produced until finally the—

(5) *Sexuparæ* appear. These are winged forms of parthenogenetic viviparous females which migrate back to the primary host. These, in turn, give rise to the—

(6) *Sexuales*, sexually reproducing male and female insects, the latter oviparous and producing the eggs, which, overwintering upon the primary host, give rise again to the *Fundatrices*.

A most complex procedure, yet simple when compared to certain other life histories among insects. The main point of interest is that man is able experimentally to control the stages of this life history by the regulation of external conditions.

The first and less complicated feature is the influence of temperature upon the period taken in the development of the *Alienicolæ* from birth to the production of the first brood. The length of this period—the Developmental period—an important factor in determining the ultimate number of insects produced, has been shown by Davidson (1) to conform to the earlier observation of Lathrop (2) on the same period in the life history of *A. pomi*. The latter worker found that the development period varied inversely as the temperature.

In the same way, the appearance of the *Sexuparæ* is controlled by external factors. Given favourable conditions, notably a sufficiently high temperature, the *Alienicolæ* continue to be produced without the appearance of males or eggs. Marcovitch

(3) obtained the reverse effect, the production of *Sexuparæ*, not only of *A. rumicis*, but of *Capitophorus hippophæs* Koch and *A. sorbi* Kalt., in June, earlier than usual, by the exposure of the plant to a short day for about seven weeks. Davidson (1) found a similar effect of external factors such as sunshine, temperature and length of day, but considered that their action on the insect was indirect via the host plant. Thus, the length of day would affect the photosynthetic activity of the plant and the carbohydrate content of the sap. This, in turn, would provoke the latent tendency of the aphis to produce the sexual forms. Marcovitch also showed that the appearance of the *Migrantes* of *A. sorbi* is governed by the increasing length of day of the spring months.

The influence of environmental factors is also shown in the production of winged forms of aphids. Rivnay (4), from the results of his own and previous work, concluded that the action of factors such as light, temperature, crowding, humidity, rainfall, growth of plant is exerted through their effect on the water balance in the body of the aphid. A reduced water content in the food of the aphid and a low atmospheric humidity cause wing development.

A second example may be taken from a quite distinct insect family, the Acridiidæ or true locusts. An explanation of the periodic locust outbreaks was suggested by Uvarov (5), from which has developed the phase theory. According to Uvarov and Zolotarevsky (6), a locust may exist in four phases, a solitary, a gregarious and two transitional phases. Given conditions favourable to an increase in numbers, the locust of the solitary phase, when it is, like the grasshopper, relatively harmless, tends towards the gregarious phase and accumulates in certain localities, notably where there is an abundance of food and shelter. Under certain conditions, the gregarious phase is reached and the swarm migrates with disastrous consequences to the vegetation on which it settles. The cause promoting the migratory flight appears to be connected with the development of the genital products, but the cessation of the migration seems to be due, not to the arrival at suitable areas for egg-laying, but to physiological causes such as the exhaustion of the fat body or the maturation of the gonads. After the migratory flight, the locust again passes through a transitional stage to revert to the solitary phase.

This theory provides a scientific basis for the combating of locust outbreaks. The discovery of the breeding grounds at which the gregarious phase is developed enables a mass attack upon the pest

prior to swarming.   As the direction of the flight is controlled by the wind, it becomes possible to forewarn regions over which the swarm will pass, enabling the prompt preparation for its destruction.

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CHEMOTROPISM

Attractants. There is now ample evidence that chemical stimuli akin to odours are important factors directing the insect to its food plants.   A classical example is due to Frisch (7), who trained honey bees to select a sugar solution flavoured with a particular flower scent from among other sugar solutions.   After alteration in the position of the solutions, the bees were able to find anew that flavoured with the odour to which they had been conditioned.   McIndoo (8) showed that the steam distillate of potato foliage attracted the Colorado Beetle, *Leptinotarsa decemlineata*, but did not identify the compounds responsible for this attraction. In the case of the Cotton Boll Weevil, *Anthonomus grandis*, Power and Chesnut (9) concluded that trimethylamine was the probable attractant, and isolated this compound and ammonia from the volatile constituents of the cotton leaf.   McIndoo (10) was doubtful whether trimethylamine had attractive properties and, indeed, whether it was possible to imitate plant odours with sufficient accuracy by chemical means.   The results of Raucourt and Trouvelot (11) suggested that the principles of potato foliage attractant to *L. decemlineata* are not water-soluble as is trimethylamine.

Perhaps the oldest example of chemotropic traps is the bottle containing a little beer hung outside the back door to catch flies and wasps.   The attractive action of beer was found by Imms and Husain (12) to rest not so much upon its alcohol as on its ester content.   The compounds of the lower fatty acids and alcohols— the esters—are pleasant-smelling compounds possessing the odour of certain fruits.   Imms and Husain found that if, to ethyl alcohol, were added small amounts of acetic, butyric, or valerianic acids, a more powerful stimulus was exercised on flies.

The correlation between attractant action and chemical constitu-

tion was studied by Cook (13). He showed that there is a definite
optimum concentration for each individual compound, which is
related to its volatility, being inversely proportional to the seventh
power of the boiling-point. Measuring the attractant properties by
the number of flies caught by the optimum concentration, he found
that attractant action decreased with rise of molecular weight of
the alcohols. With the esters, there was a similar decrease with
rise of molecular weight, but the addition of a CH_2 group to the
fatty acid radical reduced the attractiveness more than its addition
to the alcohol radical. Cook did not determine the species of fly
caught and, although his figures may have been affected by a
fractionation of the species, they are sufficient evidence of the
potential value of such studies.

The chemotropic action of fermenting sugars has been utilized
to assist the correct timing of spray applications against Codling
Moth *Cydia pomonella*. It is assumed that the number of moths
caught reflects the total number present, whereby the dates of
maximum numbers are determined and the most suitable dates for
applying contact or stomach poisons against the newly-hatched
larvæ are deduced. Eyer and Rhodes (14), from an investigation
of the chemical changes of fermenting molasses, concluded that ester
formation was again the prime factor of attraction. Carbon
dioxide and ethyl alcohol were shown to be important secondary
factors whereas acetic acid proved a repellent. The attractant
action of the baits was increased by yeast and was rendered more
permanent by the addition of preservatives such as sodium ben-
zoate.

Chemotropism also appears to be the mechanism controlling the
movement of the males of certain fruit flies. Howlett (15) showed
that the movement of the males of *Dacus zonatus* Saund. and of
D. diversus Coq. was affected by oil of citronella. *D. diversus* was
attracted by *iso*-eugenol, *D. zonatus* by methyl eugenol, both con-
stituents of this essential oil. It was at one time thought that the
odour was emitted by the females as a direct sexual guide, but
Howlett showed this to be improbable. It is possible that the
odour serves as an indirect sexual guide to the plants upon which
the females normally breed. In the Gipsy Moth *Lymantria dispar*,
Collins and Potts (16) showed that the unmated females exert a
chemotropic action on the males and they devised methods utilizing
this phenomenon for the trapping of males.

The attractant properties of essential oils have been used to trap

Japanese Beetle *Popillia japonica*, geraniol and eugenol being the most effective compounds. Van Leeuwen and Metzger (17) described a type of trap by means of which nine million beetles were destroyed by 500 traps on an area of 15 acres in 1929. The presence of traces of impurities enhances the attractivity of geraniol for which a specification was proposed by Metzger and Maines (18).

Another use of chemotropism as a pest-control measure is the employment of chemicals which stimulate the female to oviposit, whereby the eggs instead of the insect are trapped. Thus, Richardson (19) observed that House Flies (*Musca domestica*) oviposited upon substances near which ammonia is volatilized. The oviposition response could be augmented by butyric or valerianic acids, both of which are products of decomposition. Crumb and Lyon (20), on the other hand, attributed the results of their trials to the presence of carbon dioxide, a conclusion not accepted by the Richardsons (21). This discrepancy was ascribed by Wieting and Hoskins (22) to differences in concentration, ammonia, for example, being attractive at low but repellent at high concentrations.

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Trap-crops. Actual plants attractive to insect pests have usually proved the most effective lures. This fact forms the basis, not only of the cruder method of employing baits such as pieces of potato for wireworm, but of the so-called " Trap-crop " method of pest control. This method is applicable mainly where the polyphagous insect has a marked predilection for a particular plant

which may, with sufficient economy, be planted with or between the rows of the crop.   The trap plant, when infested, may either be collected and destroyed or be left to prevent the infection of the crop proper.

MacDougall (23) found that the weevil *Cryptorrhynchus lapathi* L., which attacks both alder and willow, preferred the former of these two hosts.   To protect the osiers from the pest, he proposed the planting of alders here and there in the osier bed to serve as traps. The weevils were destroyed by a timely cutting away and burning of the infected branches and twigs.   The preference of wireworms for wheat seedlings was used by Petherbridge (24) to lessen their attack on sugar-beet by the planting of wheat between the sugar-beet rows.

A marked preference by the pest for the trap crop is not always necessary.   Thus to protect the main crop of swedes from the attack of the Swede Midge (*Contarinia nasturtii* Kieff), Taylor (24a) proposed the planting of decoy rows on the headlands of the field.   The midge lays its eggs on the first available host and the decoy rows, after the eggs have been laid and the midge has died off, are lifted and destroyed.   The main crop is, in this way, protected from attack when young and enabled to grow to the stage when it can withstand the attacks of later broods of the midge.   It has been claimed that a Flea-beetle attack upon the germinating turnip seed may, at times, be frustrated by sowing with the turnip some mustard seed. ·The mustard germinates first and is said to attract the Flea-beetles from the young turnip seedlings.

Belyea (25) for the control of the White Pine Weevil (*Pissodes strobi* Peck) advised the planting, with the white pine, of Scotch pine which acts as a trap and reduces the infestation of the white pine.   Graham (26) has ascribed this result to the choice by the pest of trees exposed to sunlight and suggested that the reduced infestation of the mixed stand is due to the shading, by other trees, of the white pine.

One factor determining the success of chemotropism for the capture of the plant's pests is the free movement of the pest, which has rendered the method applicable mainly to insects.   The possibility of the utilization of chemotropism against bacteria is suggested by Hiltner's (27) theory of the chemotropic attraction of the nodule bacteria by root-hair secretions of the Leguminosæ.

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Repellents. The attraction of organisms to the plant by its odour is an example of positive chemotropism—the opposite, the repelling of the organism by the plant, has also received attention. Though negative chemotropism is not the basis of methods for trapping the pest, it may well be dealt with here because of its relationship to attractant action.

An early application of repellents is found in the old-time preventives of plague, e.g. cinnamon and camphor. As it is now known that insects are the carriers of many of the diseases classed in those days as plagues, the success of aromatic-smelling herbs may have been due more to the repulsion of the insect rather than to a disinfectant action. Nowadays, naphthalene or *p*-dichlorbenzene, the active ingredients of the familiar moth balls employed against Clothes Moths (Tineidæ), are the commonest example of the use of repellents.

In the discussion of "Deterrent Action," mention was made of uses of this control method for germinating seed. It is unknown how the insect pest discovers its host at this stage. Evidence points strongly to a positive chemotropic action, though the concentration at the germinating seed might result by the cessation, at the host, of an aimless wandering of the organisms. If due to a definite attraction, it should be possible to prevent this action either by masking the attractive smell or by the use of a definite repellent.

An example of attempts to protect the germinating seed by means of a noxious-smelling chemical is the claim that seed treatment with turpentine or paraffin will ward off the attack of Fleabeetles (28). Newton (29) tried numerous strong-smelling substances such as pyridine, turpentine and cresol derivatives, but obtained no definite indication of their repellent action. Nicotine and nicotine sulphate were more effective. On the other hand, Jenkins (30) found that, under favourable conditions, the treatment of turnip seed with paraffin or turpentine did reduce attack. A seed-dressing compounded of naphthalene and *p*-dichlorbenzene in kerosene solution was recommended by Walton (31) for Flea-

beetle control. Jarvis (32) obtained satisfactory results by sowing, between the rows of young sugar-canes, sawdust soaked with " dehydrated tar." The powerful smell kept off the larvæ of *Metaponia rubriceps* Macq. until the sets were of sufficient size to thrive despite attack.

It is an old practice to drag elderberry twigs over the germinating turnip field to drive off the Flea-beetle, but success may be due, not so much to repellent action or to the masking of the smell of the mustard oils liberated during the germination of the turnip seed, but to the deterrent action of the dust raised in the process. Newton, however, found in his trials that whereas the entire seed of the untreated plot failed, he obtained an approximately 50 per cent. " plant " on the plot treated with a steam distillate of elderberry flowers.

The use of repellents to protect foliage from leaf-eating pests is illustrated by the work of Guy (33) who, following up an earlier observation by W. H. Tisdale, examined the repellent properties of the thiuram sulphides. He selected tetramethyl thiuram disulphide, $(CH_3)_2N.CS.S.S.CS.N(CH_3)_2$, for further trial and, by the addition of supplements to improve retention, devised a spray giving a high degree of protection from Japanese Beetle, *Popillia japonica* (34). This example would have been mentioned under Deterrent Action (p. 228) but for Guy's comment on the small amount of feeding which occurred and which he attributed to incomplete coverage.

The possibility of the use of plants themselves as repellents is suggested by Schreiber's observation (35) that *Pieris brassicæ* never oviposits on cabbages surrounded by tomatoes, and by the old practice of sowing onions with carrots in order that the latter shall remain unattacked by Carrot Fly, *Psila rosæ*.

Of the use of repellents against higher animals, a familiar example is the protection of young fruit trees from rodents by painting the stems with a sulphur-linseed oil preparation. The sulphated oil, incorrectly called a sulphonated oil, is prepared by heating linseed oil to about 270° C. and slowly and carefully adding 10 per cent. by weight of sulphur (36). Rabbits will not gnaw bark treated with this preparation which appears to be harmless to the trees.

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PHOTOTROPISM

The attraction of light for moths was employed, in 1787, by Abbé Roberjot (see 37) for the trapping of Vine Moths (*Clysia* spp. and *Polychrosis* spp.). Since that time, many applications of the method and forms of light traps have been employed against the nocturnal Lepidoptera.

The first question is why these insects, normally negatively phototropic, for their nocturnal habit would indicate a dislike of light, should be attracted at all. No reason has yet been suggested though a related phenomenon has been observed by Hewitt (38). The Army Cutworm (*Euxoa auxiliaris* Grote) is negatively phototropic, remaining in broad daylight below the soil surface ; at sunset it appears at the surface and becomes positively phototropic, moving westerly towards the sun.

The attractant action of light is dependent on its nature, for Perraud (39) found, of monochromatic light, the relative attractant figures were, yellow 21·3, green 13·8, red 11·3, blue 3·9, and violet 2·3, as against 33·3 for white light. Dewitz (40) stated that diffused light was, on the whole, found more attractant than a naked light. Modern vineyard practice would appear to favour the use of acetylene light traps.

Criddle (41) questioned the efficiency of light traps because of the large proportion of males amongst the insects caught and because many of the females have already laid their eggs. Dewitz (40) found that the percentage of females attracted is dependent upon the family of Lepidoptera concerned. Of the Bombycidæ, the percentage of females caught was but 4, of the Noctuidæ 19, Geometridæ 27, and Tineinæ 39 per cent. A similar result was obtained by Theobald (42), who found that the preponderance of ·males over females applied chiefly to the Bombycidæ, Geometridæ and Tæniocampæ, but that large numbers of female Tortricidæ, Crambidæ and Tipulidæ were caught. Turner (43) found that of the total number of moths caught, those of the period 8 p.m. to 10 p.m. included 40 per cent. of the total of gravid females and

19 per cent. of the total males. In the period 10 p.m. to 4 a.m. the relative numbers of gravid females decreased whilst that of the males and spent females increased.

The second criticism advanced by Criddle was that weather conditions favourable for trapping were rare. It has been found generally that moonless, warm and still nights were necessary. In heavy rain or windy weather, Theobald found but few moths were caught and that the period of maximum catches was from June to October. From October to March, practically all the moths caught were males, but not, unfortunately, of the Winter Moth (*Operophtera brumata* (44).

A further objection raised by Criddle to the use of light traps was the danger of ensnaring beneficial Hymenoptera. Theobald found that such captures were few in number.

In general light traps are of limited usefulness. Theobald concluded that they are to be recommended only against the Tortrices in England. Against other moths the captures were too few to warrant a suspension of spraying. An objection to their use is the amount of labour involved, for the lamp and trap need daily attention and the removal of the trap during daytime is necessary to avoid the destruction of hive bees.

Phototropism is probably concerned in the observation, by Folsom and Bondy (45), that heavy infestations of *Aphis gossypii* Glov. often follow the application of calcium arsenate to cotton. Moore (46) also found that aphides tend to accumulate on potatoes sprayed with Bordeaux mixture. He attributed this result to the greater reflection of light from the sprayed leaves and showed that the response of the aphides followed the inverse square law of light intensities. He suggested that it would be profitable to include dark colouring matter in sprays and dusts used in crops liable to aphis infestation.

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STEREOTROPISM

The tendency for insects to come to rest against a solid surface is a stereotropic response. It is related, in most cases, to the desire for shelter whilst the insect is inactive and is illustrated by the manner in which many insects overwinter in cracks and loose bark.

This tendency is utilized in various forms of traps, the simplest of which is the flat board employed for the capture of slugs. For the supplementary control of Codling Moth (*Cydia pomonella*), advantage is taken of the fact that the larvæ, emerging from infected fruit on the tree or ground, wander in search of suitable quarters to pass the pupal stage. Bands of dark-coloured sacking or straw are therefore tied to the tree trunk at midsummer and are periodically examined and the pupæ found destroyed. Other suitable quarters, such as loose bark, should be removed. Large numbers of Apple Blossom Weevil, *Anthonomus pomorum* (L.), Curt., which also descend the tree trunk in late May and June to find shelter, were caught by Massee and Beshir (47) by this means, the banding material used being corrugated cardboard.

Corrugated cardboard as a banding material has also been used for Codling Moth traps, for wet sacking is to some extent repellent to the larvæ. The cardboard band should be protected from rain by attaching strips of waxed paper. A difficulty with paper bands is that they are often badly torn by birds and field mice and may be prematurely destroyed. Greenslade and co-workers (48) experimented with cardboard bands impregnated with various chemicals, which must be repellent to birds yet non-repellent to Codling Moth larvæ and Apple Blossom Weevil and must not be injurious to the tree. Solutions of certain grades of chlorinated naphthalenes in trichlorethylene were found to be of promise, but the many factors involved created difficulties in obtaining concordant results in different seasons, and, in some circumstances, the untreated bands were the more effective traps.

Under climatic conditions when a second generation of Codling Moth may develop, frequent inspection of the band traps is necessary throughout midsummer. For this reason, Siegler (49) proposed the enclosing of the band by a wire screen of a mesh which will permit the entry of the larvæ while the moths are retained. This device would also allow parasitic insects present in the larvæ to escape. The impregnation of the band with a chemical toxic but

non-repellent to the larvæ has also been recommended. Siegler and his co-workers (50) found that a satisfactory material was beta-naphthol in a non-volatile solvent such as lubricating oil. Steiner and Marshall (51) selected alpha-naphthylamine and beta-naphthol, water-soluble derivatives being found unsatisfactory.

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MISCELLANEOUS TRAPS

Included in this category are the many mechanical devices employed for the capture or imprisonment of the pest, in which advantage is taken, not so much of the tropic responses of the pest as of some peculiarity of its habits. Thus, the baited rat trap might be regarded as dependent in action upon the chemotropic attraction of the rat by the bait. The snare would then be dependent upon the habit of the pest of forming " runs " for the traversing of dense vegetation.

An example is " Grease-banding " which depends on the habit of the wingless female of Geometrid moths of crawling up the trunk of the tree to deposit its eggs on the buds and twigs. Moths of this group include the Winter Moth (*Operophtera brumata*), the Mottled Umber Moth (*Hybernia defolaria* Cl.) and the March Moth (*Erannis æscularia* Schiff.), all fruit-tree pests. The ascent of the female is arrested and the moth may be caught by placing a ring of adhesive material round the tree trunk.

The grease employed must remain sticky at winter temperatures and must be resistant to rain. Various recipes have been proposed for the making of the grease, resin in castor-oil solution being a frequent basis, but tree-banding compositions in general use are all proprietary products (see 52).

The tree trunk is first scraped to remove loose bark at a point not too near the ground, for not only may dirt be splashed up and

provide a passage across the grease but the winged male moths are able to carry the females *in copulâ* for short distances (53). The use of grease bands in bush plantations is not always successful because of the low position of the bands. Further, leaves must be collected from the bands and the surface renewed from time to time. The bands must be in position as soon as possible after leaf-fall. It is better that the grease should have no repellent action causing the moths to oviposit below the bands. If so, the area below the band should be sprayed, in early spring, with an egg-killing wash. The status of grease-banding in Winter Moth control has been discussed by Jary (54).

A second example is the " disc " method, employed against the Cabbage Root Fly (*Phorbia brassicœ*). The fly lays its eggs just below ground level near the main root of the cabbage. To prevent oviposition near the plant, tarred felt discs are placed around the stem (55). The soil should be in a friable condition permitting a close contact with the disc. It is reported that in Holland (56) the employment of such discs, of which nearly one million were distributed in 1923, reduced infestation by *P. brassicœ* from 90–95 per cent. to 5–8 per cent.

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POISONS FOR USE IN TRAPS AND BAITS

As the choice of poisons for baits and traps against insects is not restricted by phytocidal considerations, the cheaper arsenicals such as White Arsenic or Paris Green are generally used. The latter is preferred when ready solubility is a disadvantage as in baits against soil pests. An attractant food material is added to overcome the repellent action of Paris Green. For wood lice (*Armadillidium* sp.) Speyer (57) found that bran was suitable, the most satisfactory proportion being 28 lb. bran to 1 lb. Paris Green.

Formaldehyde has been employed as a stomach poison for the control of flies. Lloyd (58) traced the somewhat erratic results previously obtained to the presence of formic acid and, to a lesser extent, methylamine. Formaldehyde to be used against flies should

therefore be neutralized with a little lime water and should be free from the fishy odour of methylamine.

Against rodents, the choice of the poison employed is regulated, apart from the factor of toxicity, firstly, by its action upon other organisms and, secondly, by the results of its action upon the rodent. As there is a risk, when using poisoned baits, of domestic animals devouring the bait, a substance relatively harmless to animals other than those which are to be poisoned should be used. Also, it is well for sanitary reasons, especially in the case of house pests such as rats and mice, that the poison should not be immediately fatal, but that the rodent should, by the action of the poison, be forced to quit its usual haunts. To fulfil these two requirements a number of rat and mouse poisons have been suggested.

Squill. The poisonous properties of the bulbs of Red Squill or Sea Leek (*Urginia (Scilla) maritima* (L.) Baker), a Liliaceous subtropical plant, have long been known. The precise nature of the rat-poisoning principles is unknown, but they appear to be distinct from the cardiac glucosides to which squill owes its medicinal properties. The latter compounds are present in White Squill, which is inferior as a rat poison. The rat-poisoning principle is water-soluble and relatively thermostable. Although destroyed by boiling with dilute acid or alkali, it can be kept for long periods without deterioration (59). O'Connor, Buck and Fellers (60) recommended, however, the product obtained by drying the bulbs at 80° C. As chemical methods of standardization are not available, these investigators suggested suitable methods for the biological standardization of red squill preparations.

The specificity of the action of Red Squill on rats and mice appears to be due to its powerful emetic action, which causes vomiting by man and animals other than rodents. It has been shown to be relatively non-toxic to poultry. Particulars of suitable methods for use have been given by Munch, Silver and Horn (61), and by Schander and Götze (62).

Thallium Sulphate. In Germany, a commercial preparation has been placed on the market under the name "Zelio," containing as the active rat poison, thallium sulphate. It is claimed that not only is the preparation, used as poisoned grain, odourless but that the rats actually prefer the treated grain, that the material is relatively harmless to domestic animals and human beings and that the poison, slow in producing death, is one which as a result of its action upon the intestines induces the rat to seek water.

The vermin therefore leaves its haunts for the open, where it dies.

Barium Carbonate has been widely employed as a rat poison in the United States. Like " Zelio " it has the advantage of being without smell and, because of its corrosive action upon the mucous membrane of the stomach, induces the rat to seek water and die in the open.

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THE TREATMENT OF THE CENTRES AND VECTORS OF INFECTION

There remain for consideration certain methods dealing more directly with the restriction of the spread of the pest, which may conveniently be classified under (I) the elimination of infection foci or centres and (II), the treatment of the carriers or vectors concerned in that spread.

THE ELIMINATION OF INFECTION CENTRES

In dealing with true parasites, it is obvious that the infected plant is the actual focus where the multiplication of the pest occurs and from which it is spread. The fundamental control method is therefore the destruction of infected plants or plant material.

General. Hand-picking is still used when labour is cheap and where the pest occurs in well-defined and clearly visible agglomerates. Examples are the collection of the colonial larvæ of the Tussock Moths (Lymantridæ) and the destruction of the eggs where they are laid in easily-seen patches, as with certain of the Bombyx Moths. The hand collection, by children, of the larvæ and adults of the Large Cabbage White Butterfly (*Pieris brassicæ*) and of the Small White (*P. rapæ* L.), or of the egg clusters of the former, is a task which is encouraged by prizes given by local Gardeners' Societies. But, even with the plentiful labour sometimes found in the tropics, it is questionable whether the expenditure involved is justified. Le Pelley (1), in a study of the economics of hand collecting for the control of *Antesia* on coffee, reported adversely on the method.

The collection and destruction of diseased plant tissue is an important means of restricting spread. For the control of the Brown Rot of stone fruits (*Sclerotinia cinerea*) the removal and burning of diseased twigs and mummified fruits is of great importance, for it is from these sources that the disease spreads in the

spring. In England, the Silver Leaf Order of 1923 requires the occupier of any premises on which plum and apple trees are growing to cut off and destroy by fire on the premises, all dead wood on each plum and apple tree before the 15th of July of every year, the purpose being to check the spread of the Silver Leaf fungus (*Stereum purpureum*).*

For the destruction of exposed pests it is possible to employ poultry as the collecting agents. Theobald (3) reported on their value in the destruction of certain orchard pests; he observed the extermination of the Pear Midge (*Contarinia pyrivora* Riley), by fowls penned under the attacked trees. For the collection of fallen fruits and leaves which may serve as sources of infection, pigs and sheep have been employed. Against the Codling Moth (*Cydia pomonella*), Le Baron in 1873 suggested that pigs and sheep should be allowed to run through the orchard in order to eat the fallen apples before the larvæ escape. Delassus (4) reported that the Olive Fly (*Dacus oleæ* Gmel.) was almost eliminated, in some localities, by the persistent collection of the fallen fruit and by turning sheep and pigs into the orchards. Fulton (5) found that five pigs per acre controlled Apple Curculio *Tachypteras quadrigibbus* Say. by clearing up the early dropped fruit. As it was only necessary to keep the pigs in the orchard for a month, the damage they caused by rooting was negligible.

The insect parasite hibernates in one or other stage of its life cycle and usually requires some suitable shelter. If this be lacking, the pest is more exposed to its enemies, both climatic and biological, and the chance of its survival is more remote. The whole system of " dormant " spraying is primarily against the sheltered inactive pest. Rubbish of all sorts, which also provides a hiding-place during daytime for night-feeding pests, should be destroyed. Grass, likewise, is the home of many injurious insects during winter. Lefroy

* To protect the cut surface, it is necessary to pay heed to the general precautions taken in pruning and to treat the wound with some protective substance. As the fungus causing Silver Leaf can attack a wide variety of hosts, the eradication of all diseased material is impossible. The fungus, however, is able to gain entry to the plant only through a wounded surface, a fact which renders its protection of great importance. Brooks and Moore (2) found Stockholm tar, the material at one time recommended, unsatisfactory and they recommended a thick white lead paint. The wound dressing should be non-injurious to bark and should leave a tough elastic film which will not crack when the wood expands or contracts. Further, it should be applicable to the wet surface, a property in which the paints are deficient. Certain types of bitumen emulsion have, for this reason, found favour in practice.

(6), for this reason, considered permanent grass a mistake in any commercial orchard, with the possible exception of cherry orchards. The destruction of any moss and lichen on the trunks further removes available shelter.

The majority of the measures which comprise " Plant Hygiene " and " Orchard Sanitation " aim at the destruction of diseased plant tissue and at the removal of any shelter for pests.

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Eradication of the Host Plant. In extreme cases when no other method is possible it may be necessary to eradicate the entire affected host plant or even crop. As an example of the method, the eradication of Mediterranean Fruit Fly, *Ceratitis capitata*, from Florida may be cited. This pest was discovered at Orlando, in Florida, at the end of March, 1929, and, within two months, was found on no fewer than 697 properties within eleven counties. Before this discovery about three-quarters of the grape-fruit crop had been picked and sent from the Orlando district and the discovery of the fly tended to accelerate shipments until a Federal quarantine was imposed on 1st May. For the enforcement of the quarantine, Florida was divided into three zones. In the infected zones, which included the area within one mile of any spot at which the fly was found, all fruit and vegetables susceptible to attack were destroyed, the planting of host plants was prohibited and all host fruits and vegetables exposed in markets and elsewhere had to be screened from attack. In the protective zones, which comprised the area within nine miles of the outer boundary of an infected zone, the cultivation of host fruits and vegetables was prohibited between 1st May and 1st November (with a few exceptions), the screening of host fruits and vegetables was enforced and the export of host fruit and vegetables was permitted only to states where the establishment of the fly was unlikely to occur. The third zone, the outside zone, embraced the whole of Florida not included in the infected or protective zones. In this zone, no mature fruit, except sour limes, was allowed to remain on the trees after 15th

June and the shipment of all host fruits and vegetables to states in which the establishment of the fly was considered possible, was prohibited. Woglum (7) recorded that, by 1st June, over half a million boxes of fruit had been destroyed and that, at the height of the eradication campaign, nearly four thousand men were employed.

These rigorous measures were successful in stamping out the infestation and, on 11th November 1930, the Federal quarantine was lifted. By the end of the year, inter-state restrictions were removed. Newell (8) stated that the cost of the campaign to the Federal government was over one and one-quarter million pounds, but, to the present, there has been no report of the reappearance of the pest in Florida.

Thorough application is the fundamental requirement for success in such a campaign and, on the large scale, it is usually to be undertaken only with the stimulus of legislative action. Essentially it is a dependent upon the simple recognition of the pest or disease, a matter not always easy. In the case of certain types of virus disease, it has been shown that there exist strains of host plant which, though infected, are not visibly affected. Such plants are called " carriers "—a term borrowed from analogous cases where human beings can act as infection centres of a disease without themselves suffering ill effects. The phenomenon was first observed in plants by Mishamura (9) with Tobacco Mosaic virus, but naturally-occurring carriers of virus diseases of potatoes (10), sugar beet (11) and hops (12) are known. The existence of carrier varieties, though providing an excellent means of escaping the ill-effects of these virus diseases, introduces difficulties in their control in susceptible varieties by eradication.

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Eradication of the Wild Host. In some cases, the pest is not restricted to the cultivated host and it is then necessary, in addition to the eradication of the host plant, to ensure the removal or treatment of all other plants liable to be attacked. Lefroy (13) gave a formidable list of wild plants which may serve as hosts for

the commoner insect foes of the fruit-grower. For example, he enumerated some twenty-one species of fruit-tree pests which feed on the Hawthorn and urged the necessity of applying the same control methods to the wild host as to the cultivated.

In many cases, such weed hosts provide for the overwintering of the pest. Pritchard and Porte (14) showed that the Septoria Leaf Spot of Tomato (*Septoria lycopersici* Speg.) can attack related weeds, such as the common Nightshade, Horse Nettle, etc., and that a careful eradication of these removes the principal means of overwintering of the disease. Similarly, the destruction of all wild cucumbers, common milkweed, pokeweed, etc., for some 50–75 yards around the field has been recommended by Doolittle and Walker (15) to break, in winter, the continuity of the Mosaic disease of cucumbers.

The question of the eradication of the weed hosts is complicated by at least two factors. The first is the existence of carriers, for Smith (16) has shown that Black Nightshade, *Solanum nigrum*, is a carrier of certain potato viruses. The second is the phenomenon of biologic forms (see p. 15). Salmon (17) quoted a large number of wild plants, likely to occur in the neighbourhood of the hop garden, which can serve as hosts for the Hop Powdery Mildew *Sphærotheca humuli*. The necessity for applying to these weeds the same measures as applied to the hop has disappeared, for it is known that the particular biologic forms infecting the weeds are unable to infect the hop.

The specialization of parasitism shown by biologic forms is, however, complicated by the phenomenon which was, at one time, accounted for by the suggested " bridging species " of host plant. Thus, with *Erysiphe graminis*, the biologic form upon *Bromus racemosus* is unable directly to infect *B. commutatus*, but if first sown upon *B. hordeaceus*, the spores of the resulting generation are able directly to infect *B. commutatus*. *B. hordeaceus* therefore serves as a bridge, affording the mildew on *B. racemosus* a passage to *B. commutatus* (18). The suggestion that the infective properties of the biologic form are modified by passage to the bridging host is now regarded as untenable and it is probable that the bridging species serves to fractionate an initial mixture of biologic forms. Nevertheless, the phenomenon shows that, despite the apparent safety provided by the existence of biologic forms, there is need for constant observation of possible wild hosts.

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Eradication of " Alternate " Hosts. A curious example of parasitism is exhibited by certain organisms which require two hosts for the completion of their life cycle. This phenomenon, known as Heterœcism, was first observed by wheat growers in the injurious influence which Barberry exerted on adjacent wheat. In 1760, though the nature of the relationship was not even understood, a law was enforced in Massachusetts for the eradication of all Barberry Bushes, " for it has been found by experience, that the Blasting of Wheat and other English Grain is often occasioned by Barberry Bushes, to the great loss and damage of the inhabitants of this Province " (19). Similar legislation followed in other of the eastern United States, but in England it would appear that the eradication of the Barberry was sufficiently carried out without legislation being necessary.

The connection between the Barberry Rust and the Wheat Rust was first demonstrated by Schoeler (20), a Danish schoolmaster, in 1818, but the existence of heterœcism, not only with this particular rust, *Puccinia graminis*, but among various other rust fungi, was established by the researches of De Bary (21).

The life history of another heterœcious rust fungus, Cedar Rust of Apples (*Gymnosporangium juniperi-virginianæ* Schw.), serves as an example. This fungus overwinters on the cedar where it causes the formation of galls. In early spring the galls form the " spore horns " or " telial sori," popularly called " cedar flowers." The teleutospores present in these structures germinate and produce promycelia with secondary spores or sporidia. The sporidia are, after a while, detached and, if blown by the wind, they fall on young apple leaves where they germinate and start an infection. On the upper surface of the infected apple leaf there appear the pycnidia, which are followed later by æcidia on the under surface. The æcidia produce the æcidiospores which, if carried again to the cedar, start an infection which results in the gall formation previously described. The important point is that, in this life history, the " alternate " host is essential for the perpetuation of the

parasite.   The pest can only develop in the presence of the two hosts, and if one be eradicated the fungus will itself in time die out.

The Cedar Rust of Apple, although observed as early as 1822, did not constitute a serious pest until about 1903–5, when the disease spread to the commoner cultivated apples, and by 1910 caused severe losses in many parts of the United States.   The eradication of cedars within a distance of half a mile of apple trees was therefore recommended (22), though, in some localities, the economic and decorative value of the cedar is a complicating factor (23).

A more extended example, the early history of which has already been discussed, is the control of the Stem Rust of Cereals (*Puccinia graminis*) by the eradication of Barberry (*Berberis* spp.).   Although legal measures were taken in the older states of America, a severe outbreak of the disease in 1916 stimulated a drastic Barberry-eradication campaign.   By 1918, concerted action was taken by some thirteen of the north-central and western grain-growing states of the United States and, since that date, it is estimated that some eighteen and a half million rust-susceptible Barberry Bushes have been destroyed (24).   The extent of the campaign for the education of public opinion may be judged from the fact that nearly five million pieces of printed matter were distributed in these thirteen states.   As a result, it is stated that the average annual loss from Black Stem Rust, which in the period 1916–20 was fifty-seven million bushels, was reduced to nine million bushels in the period 1926–30.

In certain European countries the decrease of the injury occasioned by *P. graminis* has likewise followed the diminution of numbers of the alternate host.   In England, as has already been mentioned, Barberry in close association with arable land is rare ; where it occurs, as in parts of Wales, the fungus is the cause of some damage (25).   Eradication of the Barberry is legally enforced in Denmark and Norway.   Lind (26) recorded that in Denmark, severe attacks of rust, prior to legal measures in 1903 enforcing the destruction of Barberry, used to occur every two or three years. These, however, were things of the past, though in a few places where the Barberry still existed the rust caused damage to the barley crop.   Under certain conditions and in certain wheat-growing districts eradication of the Barberry is not completely successful in controlling the rust.   The life history of *P. graminis* is essentially similar to that of *Gymnosporangium* ; the teleuto-

spores, formed on the cereal host, germinate in spring, producing promycelia and sporidia which are unable to infect wheat, but if carried by wind to the Barberry produce the pycnidia and æcidia. The æcidiospores, if carried to some susceptible cereal host, start the rust infection and give rise to the uredospores. These are produced in enormous numbers and are responsible for the extensive spread of the rust among the cereal host. Later in the season, the teleutospores are again produced.

It would appear that in the case of Stem Rust, the fungus is not completely dependent in all countries on the presence of Barberry. Thus in Australia and South Africa, the rust is the cause of serious damage even though the Barberry is rare or absent from these regions. In these cases the fungus appears to be able to survive despite the absence of the æcidial stage, and it is usually assumed that the fungus here overwinters in the uredo-stage on wild grasses. Lind (26) traced a line dividing regions in which such persistence of the uredospore is impossible and in which, therefore, Barberry eradication is a complete means of control, from those countries in which the uredospore is able to overwinter and in which Barberry eradication is not of such prime importance.

There still remain, however, certain localities in which rust is often the cause of great loss yet where the overwintering in the uredo-stage is improbable. In India, for example, the uredospores cannot survive the intense heat of the plains, and in Canada there is a long break in the wheat crop. In such cases it is probable that the appearance of the disease is the result of infection wind-borne from the foothills of the Himalayas, or from the rust-infected areas of more southerly parts of America.

This probability has been investigated by epidemiological studies. Stakman, Levine and Wallace (27), for example, on the assumption that, where Barberry eradication has been carried out, the source of inoculum is from Mexico and Texas, have annually surveyed the physiologic forms overwintering in this region. In 1926, the form most common in Texas was that designated 11 ; the forms prevalent in the north were 18 and 36 and it is therefore unlikely that the original infection was wind-borne. In 1927, the forms 18 and 21 were widely distributed from Texas northwards and it is probable that the rust epidemic in the north was due to wind-blown spores. In 1928, the uredo-stage did not survive in Texas and there was no widespread damage caused by Stem Rust in the spring wheat region of the United States in that year. These results suggest

the great potential value of surveys of the biologic forms of *P. graminis* in foretelling the probability of epidemics under the conditions of the wheat-growing districts of America.

Much speculation has been provoked as to the origin of heterœcism and the reasons for the success of what, at first sight, appears such a severe handicap to the perpetuation of the species ; its survival depends upon an accidental deposition upon the right host plant twice in life. The alternate hosts of such fungi are, however, invariably members of the same plant society and, by the convenient method of overwintering thus provided, the survival of the pest is ensured. In the case of *P. graminis*, Waterhouse (28) indicated that, upon the alternate host, new biologic forms may arise by hybridization. This discovery, which has been confirmed by Stakman (29) and by Newton (30) and their co-workers, creates another strong reason for the eradication of the alternate host.

Heterœcism and the attendant method of control, by eradication of the alternate host, is not confined solely to the fungus pests. The example of *A. fabœ*, in the development of which two hosts play a part, has been mentioned on p. 311. With certain aphides this migration would appear to be obligatory, with others occasional or optional ; with all migratory forms, however, dependence upon a second host plant provides a means of checking their development and spread. But better examples of heterœcism as the basis of control are to be found in medical and veterinary entomology, such as Liver Fluke (*Fasciola hepatica* L.), which has, as its alternate hosts, the sheep and the snail *Limnœa truncatula*. Most of the tapeworms alternate in their life history between two hosts ; the Pork Tapeworm (*Tœnia solium* Rud.) passes from the pig to human beings, and is the possible cause of certain religious restrictions of the consumption of pork. Amongst other organisms there are the protozoa (*Hœmamœba* spp.) responsible for malaria, the alternate host of which is the Anopheline Mosquito ; the Trypanosomes causing the Surra disease, the Nagana disease and the Texas fever of cattle. As however in such cases the success of the heterœcious habit depends on dissemination of the parasites by the alternate host, these pests are considered in more detail in the discussion of " Insect Dissemination."

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THE ELIMINATION OF INFECTION VECTORS

It is possible to classify pests in an incomplete manner by the way in which they are transmitted from host to host, i.e. by what vector the spread of the pest is accomplished. The higher animals and many insects possess individual powers of locomotion which, assisted in many cases by their tropic responses, are sufficient to secure an adequate spread. Other lower animals and plant pathogens are dependent for that distribution on more or less accidental agencies, such as currents of air or water, and sometimes on more specialized agencies. They may, for example, invade the seed of the host and become distributed by the means employed by that host for the dissemination of its seeds. In this way arise the seed-borne diseases, the control of which has already been discussed under Seed Treatment. Further, they may be spread by the pollinating or other insect visitors of their host; or, they may secure a sufficient spread by the agency of higher animals or by the cultural operations of man himself.

Considering in more detail the various vectors responsible for pest dissemination and dispersion, we have :

Wind Transmission. In general, any dispersion of pests by wind is uncontrollable ; Butler (31), however, suggested that " wind breaks " may be of use in checking the spread of wind-borne plant diseases. He observed that, in tea gardens, those bushes to the leeward of a wind barrier suffer less from leaf diseases than those freely exposed to the wind.

In certain tea-growing districts leguminous plants are used for green-manuring. As an incidental result, it has been found that the tea shrub is appreciably protected from infestation of *Helopeltis theivora*, a capsid bug which is the cause of " Mosquito Blight." Hart (32) concluded that *Leucœna glauca* Benth., grown as a thick

hedge between the rows of tea-bushes, was more effective for this purpose than *Tephrosia* and suggested that the green-manuring crop acted as a mechanical shield against the successive waves of infestation from a focus of *Helopeltis*. He considered that *Leucœna*, however, may produce some substance unfavourable to the development of the pest or that its effect may be due to the action of *Leucœna* as a manure in strengthening the tea plant.

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Water Dissemination. The distribution of the plant's pests by water is of great importance where watering or irrigation is necessary. It is especially important in glasshouse cultivation where the partial sterilization of the soil is practised. Every effort is therefore necessary, once the soil-borne pests have been killed by the sterilization treatment, to secure freedom from re-infection, for, if accidentally introduced, the pest, freed from the competition of other fungi and insects, thrives at an alarming rate.

Bewley and Buddin (33), at Cheshunt, traced severe outbreaks of the " Damping-off " and " Buck-eye Rot " of tomatoes (*Phytophthora cryptogea* and *P. parasitica*) to an infected water supply. An examination of the various waters available in the commercial nursery showed that water from the main and from deep artesian wells was relatively free, but that water from wells receiving surface-drainage water contained large numbers of plant pathogens.

For the treatment of an infected water supply, Bewley suggested either filtration or sterilization by heat or chemicals. Filtration proved effective but this efficiency was found after a time to be reduced. As regards sterilization, of the chemicals tested, mercuric chloride and a trade disinfectant " Chloros " proved the most toxic to fungi. Mercuric chloride suffers from the objection that, being highly poisonous, special precautions are necessary to prevent human consumption of the treated water. Sterilization of the water was achieved by heating to boiling point by arranging that the pipes to the water tank passed through the boiler of the glasshouse. Bewley found sterilization of the water advisable for use in the early stages of propagation of tomato plants, the more mature plants being able to withstand better the " Damping-off " diseases. Later, Bewley (34) introduced the use of Cheshunt compound (see p. 133), the solution of which is used for watering

and which acts as a partial sterilizer, not only of the soil, but also of the water.

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Insect Dissemination. The realization of the importance of insect vectors in the transmission of diseases arose from Waite's demonstration (35), in 1891, of the spread by flies and wasps of " Fire Blight," a disease of pomaceous fruit trees due to *Bacillus amylovorus*. The diseases concerned must necessarily be confined to the smallest of parasitic organisms belonging mainly to the bacterial, protozoan and virus classes and it is on the latter group that interest has mainly centred. In only a few instances has the transmission of a virus through the true seed been established and, apart from the vegetative reproduction of diseased plants, the chief agency spreading the virus from plant to plant has proved to be insects. The insect transmission of virus has served as the spearhead of research on the virus diseases and has a rich literature surveyed by Storey (36), Bawden (37) and others (38).

Insects may be mechanical disease vectors as in Fire Blight mentioned above, when the insect serves merely as a means of conveyance though it may also provide, in the wounds it produces in plant tissues, a point of entry for the pathogen. But in other cases and particularly with the viruses the successful distribution of the disease can only be achieved by a limited number of insect species. Curly Top of Sugar-beet is disseminated only by the leaf-hopper *Eutettix tenellus* (39) ; Aster Yellows only by the leaf-hopper *Macrosteles divisus* Uhl. A specificity of the same type appears in the general rule that one species of insect can transmit but one virus, a rule which breaks down in the Aphididæ. Further Storey (40) drew attention to a group specificity between viruses grouped according to symptoms and the insect families ; thus the Mosaic viruses are transmitted mainly by aphides, the Yellows by leaf-hoppers. This correlation may be due to the manner in which the insect accomplishes inoculation for Dykstra and Whitaker (41) showed that, among even the aphides, certain *Myzus* spp. readily transmit Leaf Roll of Potato whereas *Macrosiphum solanifolii* Ashm. generally failed to do so ; the *Myzus* spp. habitually fed in the phloem whereas *M. solanifolii* often fed in the vascular tissues. But other evidence points to a more specific relationship between

vector and virus. It is now established that, in many cases, an incubation period is necessary before the insect, after feeding on a diseased plant, can become infective to a healthy plant. An early example is due to Kunkel (42) who found an incubation period of ten days in the transmission of Aster Yellows by *M. divisus*. The reason for the incubation period is not known but probably it is the time required for the passage of the virus from the alimentary canal to the salivary glands of the insect. Rand and Pierce (43) suggested that the interval was the period required for the virus to multiply in the insect host to a point when an infective dose can be emitted. This hypothesis, which suggests a symbiosis between virus and insect and hints at heterœcism, has been widely discussed (see 36) and conclusive evidence is still lacking.

It is certain, however, that the insect plays an important part in the " overwintering " of the disease organism. The carrying-over of the virus of " Curly Top " was studied by Carsner and Stahl (44). As the disease can only be transmitted by *E. tenellus* and as they showed (45) that the insects reared from eggs are non-virulent, these workers concluded that the appearance of the disease in spring is due to the presence of insects, viruliferous as a result of feeding upon the preceding year's crop, upon susceptible weeds, or on old beets growing in the neighbourhood. It is significant that *E. tenellus* is one of the few Jassids which overwinter as adults.

The control of these diseases passing between insect and plant hosts rests in general, therefore, upon two main processes, the destruction of infected plant material and the inhibition of the effectiveness of the insect concerned. An illustration is the so-called deterioration of the potato. The falling-off of yield and the general unsatisfactory results following the practice of continually growing home-grown " seed " in certain localities, was originally attributed to a number of factors. One hypothesis suggested that the potato, a plant of cold climates, deteriorated through an over-ripeness of the seed when grown under warm conditions. Brown and Blackman (46) showed, however, that neither early lifting of the seed nor the shading of the plant lifted for seed affected crop yield, provided virus diseases were absent. Alternatively, it was suggested that continued asexual propagation was responsible for deterioration. The saffron crocus, because of its irregular chromosome complement, is sterile and the cultivated variety has survived for nearly four thousand years despite continued asexual propagation (47). The theory now generally accepted is that deterioration is the result of

the accumulation of virus diseases.   The control of deterioration therefore becomes an efficient eradication of those plants showing symptoms of virus infection and, as far as practicable, the control of the insects responsible for the spread of these diseases.   Brown and Blackman (46) found that rogueing was effective in restoring the cropping vigour of a deteriorated potato crop.   Further, in districts where for climatic or other reasons the insect vectors are scarce, the rate of deterioration is slow.   For this reason, potato-growers in the south of England in general prefer Scotch seed, the lowland farmers of N. Wales secure their seed from farms at a higher elevation.   Maldwyn Davies and Whitehead (48) have shown, by an epidemiological study of the aphides of the potato crop, the relative importance of factors such as the production of winged aphides, the extent of their migration and its dependence on wind and other weather conditions, and the development of the aphis population following colonization, in determining the spread of virus diseases.   Their work has provided a scientific basis for the selection of areas suitable for seed potato production.

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Cultural and Accessory Vectors.   In the production of crops, the processes of cultivation may themselves be responsible for the dispersion of pests.   A surprising number of agencies have been found, not only amongst the implements and materials used, but also in connection with methods of transport and marketing. International exchange of plant products and nursery stock is an

outstanding example. Although in this case it is obvious that the plants themselves are the carriers, yet other factors such as methods of transport, packing, etc., are sometimes involved.

General cleanliness of implements is desirable at all times, but its value in avoiding the spread of disease is often overlooked. In glasshouse cultivation, especially during and after the process of soil sterilization, the spades, wheelbarrows and forks, contaminated with untreated soil, may easily bring about a re-infection. As regards machinery, Leukel (49) established the fact that an infected threshing machine was causing the spread of the " Purples " of wheat (*Anguillulina tritici*) among farms of a certain threshing ring. In horticulture, the pruning knife may prove a dangerous carrier, especially of the bacterial and virus diseases. Attention is to be directed to the spread of disease by marketing infected products. The use of returnable baskets, in the marketing of fruit, is objectionable because of the risk of their carrying disease to other orchards and nurseries (50).

Glasshouses may be infected unwittingly by nursery workers carrying disease organisms upon their boots, clothing or hands. Bewley (51) recommended that assistants working in diseased glasshouses should not enter houses where healthy plants were growing until their hands had been washed and their clothes either stoved or exposed to direct sunlight. An extreme case arises through the high infectivity of the virus causing Tobacco Mosaic. Valleau and Johnson (52) found that the drying of tobacco at 165° F. for forty minutes did not reduce the infectivity of diseased tobacco, and it has been suggested that the mosaic virus carried on the fingers of cigarette smokers may prove dangerous to other susceptible plants such as tomato.

Farmyard manure has been found responsible for the introduction and spread of pests. Bewley showed that straw manure may reasonably be regarded with suspicion and, in one instance (53), traced the introduction of Cucumber Anthracnose (*Colletotrichum lagenarium* (Passr.) Ell. and Hals.) to this source. The alarming rate of spread of Flag Smut of Wheat (*Urocystis tritici* Koernicke) within recent years in New South Wales was attributed by Clayton (54) to its presence in straw manure. As the spores of the fungus are not killed by passage through the alimentary canal, he suggested the substitution of oat for wheat in the horses' ration. McKay and Pool (55), in an investigation of the transmission of the Leaf Spot of Beet (*Cercospora beticola*), found that the fungus was apparently

destroyed by passage through the alimentary canal. The greatest danger of infection was found to exist in the uneaten portions of the beet which become mixed with the manure. As the organism is also destroyed by heat, these workers suggested that the safe procedure is to make ensilage of the green beet tops as the organism is unable to survive the temperature of this process.

By far the most important vector of disease is the plant itself, for it is almost exclusively upon the living plant including cuttings, bulbs, fruits, and seeds, that diseases and pests are carried over long distances. Instances of an epiphytotic following the importation of infected plants into a region previously free from the scourge are innumerable. The reasons why such outbreaks may be viewed with alarm have been discussed under " Biological Control."

Thus the steady improvement in transport facilities was held by Jensen (56) to be a not altogether unmixed blessing. He correlated the appearance in Europe, about the year 1840, of Potato Blight (*Phytophthora infestans*) with the introduction of the speedier steamship for transoceanic traffic. The fungus, a native of the northern Andes, is killed by exposure for even short intervals to a temperature not many degrees above that of a normal summer in temperate climates. In the days before steam navigation, infected tubers would be sterilized by heat during the period taken by the sailing ship in crossing the tropics, either in the passage to North America or to Europe. The introduction of the steamboat enabled a crossing of the equatorial zone in a time insufficient to ensure a complete destruction of the hyphæ in infected tubers, and the fungus was thus able to survive the transportation from its native home to both Europe and North America. Jensen's hypothesis has been criticized by Reddick (57).

Unrestricted import of plant material is undoubtedly to be regarded as a menace, and to safeguard against the importation of infected plants, legislation is the only practical measure. This may be an actual prohibition of the importation, from an infected region, of the plants or parts of plants liable to act as carriers of any particular organism. In Egypt, for example, by Law 1 of 1916, there is a specific prohibition of importation of cotton plants and seeds, cotton ginned and unginned, and of cotton wool.

Alternatively there may be inspection of all or certain plant material, together with, in some cases, fumigation or quarantine and the destruction of infected material. By the Government Order of 1917, no plant other than fruit, vegetable or sugar-cane

may be imported into British India unless sterilized with hydrocyanic acid gas at one of the specified ports. In the United States, the Federal Quarantine Act of 1912 provides for the quarantine of imported plants and the destruction of all material suspected of infection.

To safeguard against the spread of pests between neighbouring countries, international as opposed to internal legislation is generally necessary. If the passage of the pest from one country to the next involves no sea voyage, it would be necessary first to restrict the points of entry in order to permit the satisfactory inspection of the whole of the imported material. In 1881, an International Phylloxera Convention of a number of European countries was held which resulted in the establishment of measures restricting the movement of vines from one country to another—measures which have done much to prevent the spread of the pest beyond certain well-marked zones.

Considered as a method of plant protection, legislative restriction of the importation of plant products involves economic and political consequences. Although the method may be applied for reasons which rest on a firm scientific basis, it may lead to retaliatory measures by exporting countries or states economically affected by the restriction. Further, the interference with the normal flow of trade may lead to resentment by purchasers with resultant changes in demand. It is impossible therefore to pursue the discussion of the economic aspects, which have been critically reviewed in a report from the University of California (58).

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